COMPARATIVE EVALUATION OF DEGREE OF CONVERSION OF ETCH-AND-RINSE AND SELF-ETCH ADHESIVE SYSTEMS USING QTH AND LED LIGHT CURING UNITS – AN IN VITRO STUDY

A Dissertation submitted

in partial fulfilment of the requirements

for the degree of

MASTER OF DENTAL SURGERY

BRANCH – IV

CONSERVATIVE DENTISTRY AND ENDODONTICS

THE TAMILNADU DR. MGR MEDICAL UNIVERSITY

CHENNAI – 600 032

2010– 2013

CERTIFICATE

This is to certify that **Dr.UMA MAHESWARI.S,** Post Graduate student (2010 - 2013) in the Department of Conservative Dentistry and Endodontics, has done this dissertation titled "**COMPARATIVE EVALUATION OF DEGREE OF CONVERSION OF ETCH-AND-RINSE AND SELF-ETCH ADHESIVE SYSTEMS USING QTH AND LED LIGHT CURING UNITS- AN IN VITRO STUDY"** under our direct guidance and supervision in partial fulfillment of the regulations laid down by **The Tamil Nadu Dr. M.G.R. Medical University, Guindy, Chennai – 32** for **M.D.S.,** in Conservative Dentistry and Endodontics (Branch IV) Degree Examination

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ACKNOWLEDGEMENT

I wish to place on record my deep sense of gratitude to my mentor **Dr. M. KAVITHA MDS.,** for the keen interest, inspiration, immense help and expert guidance throughout the course of this study as Professor & HOD of the Department of Conservative Dentistry and Endodontics, Tamilnadu Govt. Dental College and Hospital, Chennai.

It is my immense pleasure to utilize this opportunity to show my heartfelt gratitude and sincere thanks to **Dr. S. JAIKAILASH MDS., D.N.B.** Professor & Guide of the Department of Conservative Dentistry and Endodontics, Tamilnadu Govt. Dental College and Hospital, Chennai for his guidance, suggestions, source of inspiration and for the betterment of this dissertation.

I sincerely thank **Dr. B. RAMA PRABHA MDS,** Professor for her support and encouragement throughout this dissertation.

I take this opportunity to convey my everlasting thanks and sincere gratitude to **Dr. K.S.G.A. NASSER MDS.,** Principal, Tamilnadu Government Dental College and Hospital, Chennai for permitting me to utilize the available facilities in this institution.

I am extremely grateful to **Mr.R.Shankar, Project Associate, Sophisticated Analytical Instrumental Facility (SAIF), IIT, Chennai** for his unconditional support to make this study feasible.

My sincere thanks to **Dr.A.Jerad Suresh M.Pharm.,PhD.,MBA., Principal, College of Pharmacy, Madras Medical College, Chennai and Mr.D.Sivakumar**

M.Sc., Lab supervisor, Dept. of Pharmaceutical Chemistry, Madras Medical College, Chennai for helping me in doing my study.

I sincerely thank **Dr. K. Amudha Lakshmi MDS., Dr. G. Vinodh MDS., Dr. D. Aruna Raj MDS., Dr. Nandhini M.D.S., Dr. Shakunthala M.D.S., and Dr. Sharmila M.D.S.,** Assistant Professors for their suggestions, encouragement and guidance throughout this study.

I specially thank, **Dr.S.Ravanan**, **MBA, PhD, Data manager, Biostatistician** for all his statistical guidance and help.

My sincere thanks to **Mr.D.Krishnamoorthy**, Librarian, Tamilnadu Government Dental College & Hospital, Chennai for providing me the articles needed for my study.

I whole heartedly wish to thank my **mother** for her patience, constant support and encouragement in every step of my dissertation.

I am always grateful to **God Almighty**, who is always beside me.

DECLARATION

TITLE OF DISSERTATION	**COMPARATIVE EVALUATION OF DEGREE OF CONVERSION OF ETCH-AND-RINSE AND SELF-ETCH ADHESIVE SYSTEMS USING QTH AND LED LIGHT CURING UNITS- AN IN VITRO STUDY**
PLACE OF THE STUDY	**TAMIL NADU GOVERNMENT DENTAL COLLEGE & HOSPITAL, CHENNAI – 3.**
DURATION OF THE COURSE	**3 YEARS**
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I hereby declare that no part of dissertation will be utilized for gaining financial assistance or any promotion without obtaining prior permission of the Principal, Tamil Nadu Government Dental College & Hospital, Chennai – 3. In addition I declare that no part of this work will be published either in print or in electronic media without the guide who has been actively involved in dissertation. The author has the right to preserve for publish of the work solely with the prior permission of Principal, Tamil Nadu Government Dental College & Hospital, Chennai - 3.

HOD **GUIDE** **Signature of the Candidate**

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This agreement herein after the "Agreement" is entered into on this day Dec 2012 between the Tamil Nadu Government Dental College and Hospital represented by its **Principal** having address at Tamil Nadu Government Dental College and Hospital, Chennai - 600 003, (hereafter referred to as, 'the college')

And

Mr. Dr. S. Jaikailash aged 38 years working as **Professor** in Department of Conservative Dentistry & Endodontics at the college, having residence address at T1, Vinoth Vetri Apartments, 37, Govindan Street, Ayavoo Colony, Aminjikarai, Chennai - 29(herein after referred to as the Principal Investigator')

And

Miss.S.Uma Maheswari aged 36 years currently studying as **Post Graduate student** in Department of Conservtive Dentistry & Endodontics, Tamilnadu Government Dental College and Hospital, Chennai - 3 (herein after referred to as the PG student and co- investigator').

Whereas the PG student as part of her curriculum undertakes to research on **COMPARATIVE EVALUATION OF DEGREE OF CONVERSION OF ETCH-AND-RINSE AND SELF-ETCH ADHESIVE SYSTEMS USING QTH AND LED LIGHT CURING UNITS-AN IN VITRO STUDY** for which purpose the Principal Investigator shall act as principal investigator and the college shall provide the requisite infrastructure based on availability and also provide facility to the PG student as to the extent possible as a Co-investigator

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10. If any dispute arises as to the matters related or connected to this agreement herein, it shall be referred to arbitration in accordance with the provisions of the Arbitration and Conciliation Act, 1996.

In witness whereof the parties hereinabove mentioned have on this the day month and year herein above mentioned set their hands to this agreement in the presence of the following two witnesses.

College represented by its **Principal** **PG Student**

Witnesses **Student Guide**

1.

2.

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ABSTRACT

Aim :

To determine the degree of conversion of one etch-and- rinse adhesive and three one-step self-etch adhesives for LED and QTH light cure units by Fourier Transform Infrared Spectroscopy (FTIR) analysis, immediately after curing and after one week of dry storage.

Materials and Methods:

A constant volume (0.01ml) of adhesive applied on the surface of the prepared KBr pellet. The adhesives were divided into 4 groups each containing 20 samples. Group I (Prime & Bond NT), Group II (Beauti Bond),Group III (Adper Easy One) and Group IV (XenoV).The samples were light cured with LED and QTH light cure units with a constant distance of 5mm from the pellet surface - 10 samples per light source in each group. The degree of conversion was calculated using the formula

Degree of Conversion = (1 – R cured / R uncured) X 100

Where, R is the ratio of aliphatic and aromatic peak intensities at 1639 cm-1 and 1609 cm-1 in cured and uncured BisGMA-based systems and the ratio of aliphatic and carbonyl peak intensities at 1639 cm-1 and 1720 cm-1 in non-BisGMA-based systems. Statistical analysis was performed using one way ANOVA test, followed by Post-hoc multiple comparisons by Tukey's HSD test and paired t test.

Results:

LED showed higher degree of conversion than QTH unit in all the groups. Group IV (XenoV)showed the highest DC. Group I (Prime & Bond NT) (etch-and-rinse) and Group III (Adper Easy One) showed no statistically significant difference in DC and Group II (Beauti Bond) the least degree of conversion. There is increase in degree of conversion after 1 week of dry storage in all the groups.

Conclusions:

The combination of "bonding agent and curing unit" had a significant effect on degree of conversion. The more efficient curing regime of LED unit and the better performance of one-step self-etch adhesives can be considered advantageous in clinical practice.

Key-words: FTIR, LED, QTH, etch-and-rinse, self-etch, degree of conversion

INTRODUCTION

Adhesion or bonding is the process of forming an adhesive joint, which consists of two substrates joined together. Dental adhesives are resin monomers solutions that join a restorative material with a dental substrate after the polymerization of monomers.

The ultimate goal of a bonded restoration is to attain an intimate adaptation of the restorative material with the dental substrate.[5] This task is difficult to achieve as the bonding process for enamel is different from that of dentin. The dentin which is humid and organic in nature makes bonding to this hard tissue extremely difficult.

When tooth structure is cut with a bur or other instrument, the residual components form a ‘‘smear layer’’ of debris on the surface.[67] As the smear layer constitutes a true physical barrier, it must be dissolved or made permeable so that the monomers in the adhesives can contact the dentin surface directly. Though different classifications of adhesive systems exist, the current adhesion strategies depend exclusively on how dental adhesives interact with this smear layer. One such strategy involves Etch-and-Rinse adhesives, through etching with a separate acid gel which remove the smear layer and superficial hydroxyapatite. The second strategy involves Self-etch adhesives, which make the smear layer permeable without removing it completely.

Recently, many clinicians have shifted to one-step self-etch systems (also named all-in-one adhesives) in which manufacturers have attempted to incorporate all the primary components of an adhesive system (etchant, primer, and bonding resin) into a single solution.

The clinical use of resin-based composites and adhesive systems involves the chemical or light-induced polymerization of monomers. The quality of the final polymer network of resin-based composites and adhesive systems has a significant effect on the properties of these restorations and their clinical performance. The overall effect of incomplete polymerization may result in materials with less than optimal clinical performance as well as the elution of components which may have an adverse effect on local and systemic functions. In addition, the adhesive-dentine interface is recognized as important in maintaining the integrity of resin-based composite restorations. In vitro studies have indicated a good relationship between degree of conversion (DC) and the mechanical properties of the adhesive with strength of bonding to tooth tissues.[4,22,45] A high degree of conversion may also reduce permeability at the bonding assembly, increasing the resistance to degradation.[7] Incomplete polymerization of adhesive monomers has been speculated as one of the reasons for the occurrence of nanoleakage.[58]

Quartz-tungsten-halogen bulbs have been used for many years as the light source to light-activate visible-light cured composite resins. Blue light emitting diode (LED) technology has been indicated as an alternative to conventional halogen lights.

Optimal monomer infiltration into the demineralized collagen network and achievement of high degrees of monomer conversion are crucial factors for establishing long-lasting resin/dentin bonding.[67] Some factors such as the residual water or organic solvents, and the quality of the light source applied to photo-activate the adhesive systems might affect the conversion of resin monomers. Although there are several reports about the effects of LED on composite resins, little-to no studies exist about the efficiency of LED on the degree of conversion of adhesive systems.[23]

Among the several methods such as RAMAN spectroscopy, FTIR (Fourier Transform Infrared Spectroscopy),EPR (electron paramagnetic resonance), NMR (nuclear magnetic resonance), DSC (differential scanning calorimetry) and DTA(differential thermal analysis)to determine degree of conversion of resins, FTIR has been proven to be an useful technique and also it has been used as a reliable method.[42]Improved optics and internal laser reference for automatic calibration have increased the sensitivity and accuracy of FTIR spectrometers.

This study evaluated the effect of LED and QTH light curing units on the degree of monomer conversion of Etch–and-Rinse (Prime & Bond NT) and one-step one bottle self-etch adhesive systems(Beauti Bond, Adper Easy One, Xeno V)using Fourier Transform Infrared (FTIR) spectroscopy analysis.

AIM:

To determine the degree of conversion of Etch-and-Rinse (Prime&Bond NT) and self- etch adhesive systems (Beauti Bond, Adper Easy One, Xeno V) with LED and QTH light curing units.

OBJECTIVES:

- ✓ To determine the degree of conversion of etch-and-rinse (one bottle system) and self-etch adhesive systems (one bottle system) using Fourier Transform Infra Red Spectroscopy (FTIR) immediately after curing with LED and QTH light curing units.
- ✓ To determine the degree of conversion of etch-and-rinse and self-etch adhesive systems after dry storage for 1week to confirm polymerization reaction continues even after 24 hrs.

REVIEW OF LITERATURE

Loshaek & Fox (1953)[52] used polymerization contraction, as a method to determine DC, is based on the fact that the number of converted methacrylate groups is the main factor determining contraction. It measures the vertical displacement of an aluminium disc due to the polymerization contraction of the resin sample in a linometer device. The linear displacement is then converted to volumetric contraction based on the assumption that the contractions are isotropical. Subsequently, the "conversion of methacrylates" is calculated using the molar volume of complete conversion and the molar volume of the sample.

Wertz (1972)[95a] conducted ESR is a technique for chemical analysis of substances, such as free radicals, with one or more unpaired electrons which is associated with molecular paramagnetism. Electron transitions can be induced between spin states by applying a magnetic field and then supplying electromagnetic energy, usually in the microwave range of frequencies. The resulting absorption spectra are based on the principle that resonant frequencies for a particular substance are directly proportional to the strength of the applied magnetic field.

Ruyter & Svendsen (1978)[70] suggested the term 'remaining methacrylate groups' and calculated as a ratio between the IR absorbance bands of aliphatic and aromatic C=C double bonds before and after polymerization.

Eliades et al. (1987)[26a] used four different terms in their study, degree of double bond conversion, degree of cure, degree of saturation and remaining carbon-

carbon double bonds, probably as synonyms to refer to monomer conversion to polymers.

Chung and Greener (1988)[17] analysed the infrared spectra of seven commercially available posterior composite resins were analysed by ratioing the C = C aliphatic peak to the C = C aromatic peak. The degree of conversion ranged from 43.5 to 73.8%. The result was similar to the range previously obtained from unfilled Bis-GMA based resins and commercial anterior composites.

Venhoven (1993)[91] studied the effect of diluting monomers (TEGDMA, MMA and HPMA) on the polymerization contraction and monomer conversion of BisGMA-based resin mixtures. The results showed that the conversion of methacrylates increased with the increasing amount of diluents, irrespective of their type.

Rueggeberg & Tamareselvy (1995)[69] in one study, the "extent of cure" of dental resins was measured by polymerization shrinkage and compared to that obtained by FTIR spectroscopy. MMA/TEGDMA mixtures with increasing amounts of TEGDMA and a commercial adhesive system were prepared as either thin films or 1 mm thick bar shaped specimens. The polymerization shrinkage was determined based on the differences in volumes of cured and uncured samples. The molar volume contraction was calculated based on the number of moles of C=C double bonds in the calibration curve. The subsequent extent of cure was calculated as a ratio of the observed shrinkage and a total shrinkage in the case of complete conversion. The results showed no significant differences between the conversion values obtained by shrinkage and FTIR methods. The authors suggested that if manufacturers disclosed

the molar C=C content and resin density of their products, researchers would only need to determine weight differences between dry and water-immersed cured material in order to calculate the DC.

Additionally, the results of this study showed no correlation between the amount of TEGDMA and DC in thin samples whereas the amount of TEGDMA in excess of 5 mol% resulted in significant decrease in DC in bar-shaped samples.

Imazato et al.(1997)[42a] studied the effect of an antibacterial monomer, MDPB, on the antibacterial activity, DC and tensile bond strength of an experimental adhesive mixture . MDPB was added in 2%, 4% or 10% concentrations to the primer of the two-step self-etch adhesive system (LB Bond, Kuraray) and the final concentrations after mixing of primer and bond were 1%, 2% or 5%. Spectra were taken immediately after curing of the primer-bond mixture placed on a potassium bromide disc of the FTIR spectrometer. Antibacterial activity against Streptococcus mutans was shown to be significantly higher in the system containing MDPB than in the control system without MDPB. The DC values were 66-69% and 61-65% and no significant differences were observed between the groups with various amounts of MDPB and the controls. Bond strength values were comparable between experimental resin mixtures and controls in both studies. The authors suggested that MDPB could increase the antibacterial potential of dentine primers without an adverse effect on DC and bond strength.

Hotta (1998)[39a] used ESR(Electron spinning resonance) to indirectly measure monomer conversion by measuring the amount of free radicals after irradiation of adhesive mixtures with increasing amounts of monomers. The amount of propagating

radicals gradually increased with irradiation time but decreased with the addition of primers.

McClelland (1998)[52a] used PAS-IR, part of the IR incident light is absorbed by the sample and converted to thermal energy which diffuses towards the sample surface. Sound pressure waves are generated at the surface and captured by a high-sensitivity microphone. The detected signal is converted into a conventional IR spectrum.

Eliades et al.(2000)[26] reported the highest DC values for a dual-cured adhesive, followed by a light-cured one whereas a chemically-cured adhesive showed the lowest DC.

Imazato (2001)[42] calculated the DC of experimental RBCs containing various amounts of TEGDMA and fillers using DTA and compared these values with those obtained by FTIR spectroscopy. Essentially, this method is the same as previously reviewed DSC. DTA resulted in slightly greater DC values (3-10%) compared to FTIR values. The authors attributed these differences to the method of DC calculation as well as to the theoretical assumption that the heat of conversion of C=C double bonds is the same for all methacrylate monomers. Furthermore, they suggested that possible reflection of the incident light at the bottom of the thermal chamber could result in an augmenting effect.

Emami & Soderholm (2003)[28] reported that the calculated DC does not indicate the actual amount of monomer converted into polymer but the percentage of converted aliphatic C=C double bonds in the resulting polymer. The DC of 60%

means that 60% of C=C bonds are converted leaving 40% of C=C bonds and not 40% of the monomer unreacted.

Calheiros et al (2004)[14] used PAS-IR to determine the DC of two hybrid and two micro-filled RBCs. The DC values were between 15% and 45% for both RBCs irrespective of the applied light energy density. The authors attributed the lower DC values in this study compared to other studies to lower sensitivity of PAS-IR compared to other spectroscopic methods, particularly FTIR and Raman.

Bang et al. (2004)[6] reported a positive correlation between the DC and polymerisation shrinkage in three orthodontic adhesives cured with a conventional halogen LCU but not with a plasma arc LCU. The conventional halogen LCU produced higher DC values in all adhesives than the plasma arc LCU.

Bouschlicher et al. (2004)[8] reported that as a measure of conversion, bottom-top ratio of KHN was approximately 2.5 times more sensitive than the bottom-top DC ratio. They stated that KHN alone cannot indicate the differences in monomer conversion in different RBCs due to variables, such as filler content. However, they concluded that the relationship between the bottom-top ratios of KHN and DC is independent of the filler content.

Yamada et al.(2004)[98] who published the first paper on commercial adhesive systems , studied the effect of mixing self-etching primers and bonding agents from different manufacturers on DC and bond strength. FTIR measurements and microtensile bond strength (μTBS) were performed 24 h after water storage at 37°C. The highest DC values were observed when self-etching primers and bonding agents from the same manufacturer were used. When self-etching primers and bonding

agents from different manufacturers were used consecutively, μTBS and DC decreased in some cases.

Kim et al.(2005)[49] investigated the effect of hydrophilic nanofillers on the DC and mechanical properties of ethanol-based experimental adhesive mixtures containing BisGMA, HEMA and 4-META. The nanofillers were added up to 3 wt% and FTIR spectra were taken immediately after curing on potassium bromide discs. Though DC values were comparable for all groups irrespective of the presence of nanofillers, mechanical properties showed inconsistent values so it was concluded that hydrophilic nanofillers did not improve the adhesive formulation.

Wunderlich (2005)[96a] used DSC which is a calorimetric technique based on the assumption that heat generated during resin polymerization is proportional to the percentage or concentration of reacted monomers.

Tanimoto (2005)[86] studied after light curing of resin-based materials, the temperature is measured using thermocouples attached to a differential scanning calorimeter. The heat of polymerization is calculated from the area under the peak of the differential temperature curve and the extent of polymerization (Ep) is calculated as the ratio of the obtained heat related to the reference values for 100% conversion. This is the theoretical amount of heat evolved during complete polymerization of the material and is calculated using the molar heat of polymerization of lauryl methacrylate .Using this method, it was shown that the Ep increases with increasing amounts of TEGDMA in UDMA/TEGDMA mixtures. The Ep of experimental mixtures decreased with increasing filler content between 0-60% but then significantly increased at 70% of the filler content.

Bae et al.(2005)[4] studied the effect of BisGMA on the DC and mechanical properties of an experimental adhesive system. A series of adhesive mixtures were prepared containing 20/80 to 80/20 wt% of BisGMA and TEGDMA, placed on a potassium bromide disc, covered with a Mylar strip and cured for 20 s. Scotchbond Multipurpose was used as a control. FTIR spectra were taken immediately after curing and after 48 h of dark storage in air at an unstated temperature. The highest DC was found in the mixtures containing 30-50 wt% of BisGMA and was comparable to the commercial adhesive. The DC of all mixtures increased after storage. The authors suggested that high DC associated with better mechanical properties was due to the high molecular weight and cross-linking potential of BisGMA. However, extreme amounts of BisGMA may restrict monomer reactivity due to high viscosity resulting in lower DC and inferior mechanical properties.

Emami & Soderholm (2005)[27] conducted a study using DSC on the effect of curing modes and initiators on the DC of BisGMA (50wt%)/TEGDMA (50wt%) mixtures. A high power halogen LCU operating at standard and soft-start modes and an LED LCU at standard mode were used. The initiators, CQ or PPD, were combined with one of three co-initiators, DABE, CEMA or DMAEMA. Standard modes of both halogen and LED LCUs resulted in higher DC values than soft-start after 10 s of light curing. Soft-start resulted in comparable DC values as the standard halogen and higher than the LED LCU after 40 s of light curing. CQ-based initiator systems produced higher DC values than PPD-based systems after 10s of light curing irrespective of the LCU and curing mode. However, all systems showed comparable DC values after 40 s of light curing.

Cadenaro (2005)[13] compared a three-step and two-step etch-and-rinse and two step and one-step self-etch commercial adhesive systems using DSC, lower DC and higher permeability values were found in two-step etch-and-rinse and one-step self-etch adhesives. Curing times, beyond manufacturers' recommended times, improved polymerization and reduced permeability of these adhesive systems.

Dickens & Cho (2005)[22] investigated the DC, mechanical properties and residual acetone content of experimental adhesive systems containing various amounts of PMGDM and HEMA. The adhesive was placed in three increments in 1 mm deep moulds and in one increment in 0.52 mm deep moulds held between two glass slides and cured through the top slide. FTIR spectra were taken immediately after light curing and after 48h of dark storage.

No differences in the DC were observed in bulk adhesives with different initial acetone content. Significantly higher DC was found for 60 s curing time and 48 h of dark storage. The DC decreased significantly with increasing initial acetone content in thin films. Computer simulation showed that residual acetone content depended on sample thickness. In thin films, the adhesive with the highest initial acetone concentration gave the least residual acetone content after drying, whereas the opposite was observed for bulk adhesives. The authors concluded that solvent removal from adhesive systems is a diffusion-controlled process dependent on solvent nature and amount as well as the thickness of the adhesive layer.

Usumez et al. (2005)[89] showed that plasma arc, high power halogen and LED LCUs produce comparable or higher DC in orthodontic lingual retainer adhesives compared to a conventional halogen LCU. The DC of the lingual retainer adhesives

was also affected by their chemical composition but the authors offered no conclusive statement as to what caused the differences in the two tested materials.

Cadenaro (2006)[12] studied the effect of dentin bleaching on DC in commercial adhesive systems and concluded that Hydrogen peroxide, as a bleaching agent, had an adverse effect on the DC whilst storage in 100% humidity at 37°C resulted in increased DC.

Wang (2006)[94] studied the effect of water and initiator systems on the polymerisation kinetics was studied in HEMA-based In this study, co-initiators DHEPT, DMAEMA, NPG or DPIC were added to water-based HEMA/CQ mixtures. The adhesive was placed on a glass slide,covered with a Mylar strip and cured for 40 s using a halogen LCU and micro-Raman spectra were taken immediately after curing. The differences in polymerization and reactivity of HEMA were observed for different co-initiators. Unlike DHEPT, NPG and DMAEMA were compatible with HEMA. DPIC had an accelerating effect on the polymerization rate. Though CQ/DHEPT is used commonly in adhesive systems, this combination did not initiate HEMA polymerization. Water had an adverse effect on polymerization.

Kim et al. (2006)[48] investigated the effect of curing time on the DC of two adhesive systems, the thickness of the oxygen inhibition layer (OIL) and the μTBS. Acetone-based three-step (All Bond 2, Bisco) and two-step (One Step, Bisco) etch-and-rinse adhesive systems were placed on a glass slide and cured using a conventional halogen LCU for 10 s, 20 s, 30 s or 60 s. The DC was calculated as a ratio between the absorbance peaks for C=C double bonds and the CH internal standard in cured and uncured samples. The DC values were in the range of 72-87%

and increased with longer curing times. A negative correlation was observed between the DC and the thickness of the OIL. μTBS obtained after adhesive and RBC application to dentine discs decreased with longer curing times. The lowest bond strength values were observed in the group with no OIL i.e. where the adhesive systems were cured through a Mylar strip. The authors concluded that an OIL with an adequate thickness is necessary for satisfactory μTBS and that manufacturers' recommended times should be followed.

Kanehira et al.(2006)[45] correlated the DC of seven all-in-one adhesive systems with their shear bond strength (SBS). SBS of human enamel samples restored with an adhesive and a hybrid RBC was measured. The DC was calculated from a different set of samples which were prepared by applying the adhesive and RBC to the ATR accessory crystal. FTIR spectra were taken immediately after polymerization and 10 min, 1 h, 2 h and 24 h thereafter. The DC increased with time after polymerization in all adhesive systems. The DC values varied significantly from 50% to 75% immediately after polymerization and from 66% to 94% after 24 h. No definite conclusion regarding the differences in DC among adhesive systems could be made due to large variations in adhesive chemical composition. A linear relationship between DC and SBS was found for all adhesive systems.

Xu et al.(2006)[97] correlated the DC and SBS of a two-step etch-and-rinse adhesive system (Single Bond, 3M ESPE) cured for 20 s, 40 s or 60 s from tip-to-surface distances of 0mm, 2.3 mm, 4.6 mm and 6.9 mm. The adhesive system was placed on a glass slide, covered with a Mylar strip, cured and FTIR were taken immediately after curing. The DC values were between 65% and 85% and a negative

correlation was observed between the curing distance and DC. SBS was measured on a different set of samples, which were prepared by applying the adhesive and a hybrid RBC to dentin discs. The same relationship was observed between the curing distance and SBS as it was observed for the curing distance and DC. It was concluded that a decrease in radiant exposure, due to the increasing distance, could be compensated by longer curing times. Curing times of 40-60 s were proposed for curing adhesives in deep and proximal cavities.

Ogliari et al. (2006)[64] studied the effect of a new co-monomer ETMA on the DC and bond strength of adhesive resins. In this study, 0.1 wt%, 1 wt% and 10 wt% of ETMA was added to a BisGMA/HEMA adhesive system (Scotchbond Multipurpose, 3M ESPE). FTIR measurement was done after 24 h of dark, dry storage. μTBS was evaluated on a different set of samples, prepared by applying the adhesive and a micro-hybrid RBC to human dentine discs. ETMA resulted in 64 comparable DC but significantly higher μTBS than the control.

Ogliari (2007)[63] studied the effect of an onium salt as a co-initiator on polymerization kinetics of adhesive resins. In this study, real-time FTIR spectra were taken during curing of a series of experimental adhesives containing CQ as the initiator and various amounts of EDAB and an onium salt (DPIHFP) as the co-initiators. The effect of co-initiators increased the reactivity of the initiator system. Comparable DC values were obtained with the two co-initiators irrespective of their concentration. The fastest rate of polymerization was observed in the system containing both co-initiators confirming the hypothesis that an onium salt improves the polymerization kinetics in an experimental dental adhesive resin.

Santos et al. (2007)[74] reported that the depth of cure was greater after light curing RBC samples with a QTH compared to an LED LCU. They identified a relatively uniform and slow decrease in hardness and DC with a sudden drop for both characteristics at 4 mm for the QTH and 3 mm for the LED LCU.

Breschi et al. (2007)[10] correlated the permeability and polymerization kinetics of adhesives after exposure to different LED LCUs. DSC measurements showed that the rate of polymerization increased with longer curing times in all adhesives. An inverse correlation was reported between the rate of polymerization and permeability of adhesives.

Lim & Lee (2007)[51] showed that the DC of orthodontic adhesives was affected by the reflectance of the background teeth and not the diffuse light transmittance of orthodontic brackets. The DC was affected by the types of adhesives, brackets, LCUs and curing protocol.

D'Alpino et al.(2007)[21] also studied the effect of LCUs on polymerization kinetics and the DC of a two-step etch-and-rinse adhesive system containing nanofiller particles (Adper Single Bond, 3M ESPE) using FTIR spectroscopy. The adhesive was applied to the ATR accessory crystal and cured for 10 s using a conventional halogen, an LED or a plasma arc LCU. The LED LCU produced the highest and the plasma arc the lowest DC values and polymerization rates.

Arrais et al. (2007)[2] studied the effect of LCU types on the DC of a two-step etch-and-rinse (Single Bond, 3M ESPE) and a two-step self-etch (Clearfil SE Bond, Kuraray) adhesive systems. A halogen at 600 mW/cm2 and an LED LCU at 400 mW/cm2 were used for 10 s. FTIR spectra were taken immediately after light curing

of the adhesive applied to potassium bromide pellet with no Mylar strip and after a week of storage in distilled water. The halogen LCU produced higher DC values in both adhesive systems, immediately after curing and after one week of storage. The initial DC values were around 27-35% and after storage increased to 50-56%. Though the self-etch adhesive showed initially lower DC, the DC of both systems was comparable after storage.

Ye et al.(2007)[38] studied the effect of LCU types and irradiance on the polymerization kinetics and the DC of a two-step etch-and-rinse (Single Bond, 3M ESPE) and two all-in-one self-etch adhesive systems (One-Up Bond F, Tokuyama; Adper Prompt, 3M ESPE) using ATR-FTIR with a real-time spectrum collector. The samples were placed on ATR accessory crystals and cured with either a halogen and or an LED LCU for 10 s, 20 s or 40 s. The real-time spectrum collector allowed continuous collection of IR spectra during polymerization. The highest initial polymerization rate and highest DC were found in the etch-and-rinse system with least solvent. Higher light irradiance accelerated curing kinetics and the resulting DC in all three systems. Adper Prompt showed the lowest DC values for all curing times, 11-20% after 10 s and 35-63% after 40 s.

Rode et al. (2007)[68] studied the DC and Vickers microhardness in an RBC cured with an LED, an argon laser or a conventional halogen LCU at various distances (0, 3, 6 and 9 mm). Both DC and microhardness decreased for all LCUs with increasing RBC thickness and curing distances. The LCUs produced comparable DC and microhardness values in samples 1 mm thick and irradiated from the maximum distance of 3 mm.

Faria e Silva et al. (2007)[31] studied the DC of a dual-cured resin cement (RelyX ARC, 3M ESPE) related to the fiber post translucency. In this study, micro-Raman spectra were taken from the top, middle and apical areas in a simulated root canal after 24 h of storage. In the latter study, a real-time spectrum collector was used to obtain FTIR spectra from adhesives applied to ATR accessory crystals. Spectra were taken continuously up to 5 min after the start of polymerization. The translucent fiber post produced higher DC values at all depths than the non-translucent one. The DC decreased with increasing depth in the root canal irrespective of the type of fiber posts.

Faria-e-Silva (2008)[32] reported the DC of light-cured, dual-cured and chemically-cured adhesive systems ScotchBond Multipurpose and Prime&Bond NT (Dentsply De Trey) were compared. In this study, light cured and dual-cured adhesive systems showed rapid polymerization during the first 30s. After 5 min, the DC was around 60% for Scotchbond Multipurpose and 50% for Prime&Bond NT. Chemically-cured Scotchbond Multipurpose showed very slow polymerization reaction and the DC of around 40% after 5 min, whereas chemically cured Prime&Bond NT showed no reaction for the entire observation period.

Sadek et al. (2008)[71] correlated early and 24 h bond strength and DC of three-step etch-and-rinse (Adper Scotchbond MP, 3M ESPE), two-step etch-and-rinse (Adper Scotchbond 2, 3M ESPE), two-step self-etch (Clearfil SE Bond, Kuraray) and one-step self-etch adhesive systems (Adper Prompt L-Pop, 3M ESPE). The adhesive systems were placed in 0.5 mm thick iron moulds, covered with Mylar strips and cured with a halogen LCU. FT-Raman spectra were taken immediately after curing,

then after 1 h and 24 h dark storage in air at 37°C. μTBS was measured on a different set of samples, prepared by applying the adhesive and a micro-filled RBC to human dentin discs. No correlation was found between the DC and μTBS. The DC was in the following order: Clearfil SE Bond (81- 87%) > Scotchbond Multipurpose (77-81%) > Scotchbond 2 (60-65%) > Adper Prompt L-Pop (37-42%). The authors concluded that very limited 'dark' cure occurred within 24 h in the studied adhesive systems.

Cadenaro (2008)[11] studied the effect of hydrophilicity and solvent content on the Ep of experimental adhesive systems. Low DC values were found in experimental adhesive systems with the solvent in excess of 50 wt%. Although the authors claimed that resin hydrophilicity had an influence on the DC , this remains unclear since the adhesive systems contained different monomer compositions rather than different percentages of the same hydrophobic/hydrophilic components.

Guo et al.(2008)[36] studied the effect of water and initiator systems on the polymerization kinetics in BisGMA/HEMA-based experimental adhesive systems and concluded that water significantly reduces polymerization but suggested that this may be compensated by the addition of onium salts. In this study, DMAEMA, EDMAB or DPIHFP were added as co-initiators in water-based BisGMA/HEMA/CQ mixtures. Real-time FTIR measurements were used to monitor polymerization. The results confirmed that the onium salt significantly improves polymerization kinetics and DC.

Miletic et al.(2009)[54] considered the term "ratio of C=C double bonds" (RDB) to be more appropriate than DC, since it refers to the ratio of carbon-carbon double bonds that take part in polymerization irrespective of the processes that may affect the

initial monomer to polymer conversion. However, it is accepted that this term may be ambiguous in certain cases, and it is suggested that, for clarity, the 'double bonds' are specifically defined in every case. Furthermore, the term 'C=C double bonds' may be inappropriate in resin-based materials, such as Filtek Silorane, which have a different chemical composition and whose polymerization is based on the opening of C-O-C rings and not C=C double bonds.

Faria-e-Silva et al. (2010)[30] evaluated the degree of conversion (DC) of bonding agents photoactivated using QTH or LED light-curing units (LCUs) was evaluated by Fourier Transform infrared spectroscopy with an attenuated total reflectance (ATR) device Two etch-and-rinse (Scotchbond Multi-Purpose–SBMP and Single Bond 2–SB2) and two self-etch adhesives (Clearfil SE Bond–CSE, and Clearfil S3 Bond–CS3) were tested. For SBMP and CSE, the primer was not used. The irradiance and spectral emission of the LCUs were obtained with a radiometer and spectrometer. The materials were placed onto the ATR cell as thin films, the solvent was evaporated (when necessary) and photoactivation was carried out for 20 seconds. The DC (%) was evaluated after five minutes When cured using the QTH unit, the DC results were SB2=CS3>CSE>SBMP; for all LEDs, the DC results showed SB2>CSE>SBMP>CS3. For SB2, the highest DC was observed when the material was cured with Radii, while there were no significant differences among the other LCUs. CSE and CS3 showed higher DC when cured using the QTH unit, but similar results were observed among the LEDs. For SBMP, no significant differences among the LCUs were detected. In conclusion, the combination bonding agent vs curing unit had a significant effect on DC, mainly for the self-etch adhesives.

Jose et al.(2011)[43] investigated the effect of a desensitizer on the degree of conversion of two bonding resins using Fourier transform infrared (FTIR) spectroscopy. An etch-and-rise bonding resin and a self-etching adhesive resin were selected for the study. Vivasens (Ivoclar Vivadent) was used as the desensitizing agent. Grouping was done as follows: Group I: Adper Single Bond (*n*=10), Group II: Adper Single Bond + Vivasens (*n*=10), Group III: AdheSE One (*n*=10), Group IV: AdheSE One + Vivasens (*n*=10). The bonding resin alone was light cured for 20 seconds in groups I and III. For groups II and IV, 1 ml each of the bonding resin and the desensitizer was mixed in a vial and light cured for 20 seconds. The specimens were analysed using FTIR spectroscopy and concluded that the degree of conversion is increased when a dentin bonding agent is used along with a desensitizer. Hence, this combination can be recommended to effectively control postoperative sensitivity.

Borges et al (2012)[7]evaluated the effect of five methods of solvent volatilization on the degree of conversion (DC) of nine one-bottle adhesive systems using Fourier transform infrared/attenuated total reflectance (FTIR/ATR) analysis. Nine adhesives were tested: Adper Single Bond 2 (SB), Adper Easy One (EO), One Up Bond F Plus (OUP), One Coat Bond SL (OC), XP Bond (XP), Ambar (AM), Natural Bond (NB), GO, and Stae. The adhesive systems were applied to a zinc-selenide pellet and 1) cured without solvent volatilization, 2) left undisturbed for 10 seconds before curing, 3) left undisturbed for 60 seconds before curing, 4) air-dried with an air stream for 10 seconds before curing, and 5) air-dried with an air stream for 60 seconds before curing. FTIR/ATR spectra were obtained, and the DC was calculated by comparing the aliphatic bonds/reference peaks before and after light activation for 10 seconds (FlashLite 1401). The DC of GO and Stae adhesive systems

was not affected by the five evaporation conditions. Air-drying for 60 seconds before curing yielded the highest DC for SB, EO, and OC. Extended solvent volatilization time (60 seconds) either with or without air-drying before curing provided the highest DC for AM, NB, XP, and OUP. Thus, the monomer conversion of adhesive systems was material dependent. In general, the 60-second passive or active air-drying modes to volatilize solvents before curing enhanced the degree of conversion for the one-bottle simplified adhesive systems.

MATERIALS AND METHODS

ARMAMENTARIUM

I. FOR EVALUATION OF DEGREE OF CONVERSION

- ✓ PerkinElmer Spectrum One FTIR spectrometer (PerkinElmer Co, Massachusetts, USA)
- ✓ Spectrophotometric-grade KBr (Potassium Bromide)
- ✓ Agate Mortar and pestle for KBr powder grinding
- ✓ Stainless steel die to prepare KBr pellet
- ✓ KBr pellet pressing machine
- ✓ Tweezers
- ✓ Micro pipette
- ✓ Teflon tube with diameter of 11 mm and height of 5mm
- ✓ Applicator tips

II. EXPERIMENTAL MATERIALS :

LIGHT CURE UNITS USED:

LIGHT CURE UNIT	COMPANY	INTENSITY	WAVELENGTH
Satelec MINI LED light curing unit	Acteon Group Ltd, Norwich UK	1250 mW/cm² ± 10%	420 - 480 nm Peak wavelength : 455 – 465 nm
CU 100 A QTH light curing unit	Rolence Enterprise Inc. Chung Li , Taiwan	500~600mW/cm2	400~500nm

BONDING AGENTS:

TYPE	ADHESIVE SYSTEMS	COMPOSITION	MANUFACTURER
Etch-and-Rinse one bottle system	Prime&Bond NT	❖ PENTA ❖ Di& trimethacrylate resins ❖ Cetylamine hydrofluoride ❖ UDMA ❖ Silica colloidal ❖ Solvent: acetone	Dentsply DeTrey, Konstanz, Germany
one-step self-etch, one-bottle	Beauti Bond	❖ Bis-GMA ❖ TEGDMA ❖ Carboxylic acid monomer ❖ Phosphoric acid monomer ❖ Acetone ❖ Water	Shofu, Kyoto, Japan
one-step self-etch, one-bottle	Adper Easy One	❖ Bis-GMA ❖ HEMA ❖ Ethanol ❖ Water ❖ Phosphoric Acid-6-Methacryloxy-Hexylesters ❖ Silane Treated Silica ❖ 1,6-Hexanediol Dimethacrylate, Copolymer Of Acrylic And Itaconic Acid ❖ (Dimethylamino)Ethyl Methacrylate ❖ Camphorquinone ❖ 2,4,6trimethylbenzoyldiphenylphosphine Oxide (TPO)	3M ESPE, St Paul, MN, USA
one-step self-etch, one bottle	Xeno V	❖ Bifunctional acrylic amides ❖ Acidic acrylic amides ❖ Inverse functionalized phosphoric acid ester ❖ Acrylic acid ❖ Water ❖ Tertiary butanol ❖ Initiator&coinitiator butylated benzene ❖ Stabilizer	Dentsply DeTrey, Konstanz, Germany

METHODOLOGY:

FTIR SAMPLES PREPARATION:

Two Strategies of adhesive systems were chosen.

A) Etch-and-Rinse - one bottle adhesive system

B) Self-etch - one bottle adhesive system

Two Different light curing sources

A) LED curing unit

B) QTH curing unit

Distribution of the samples:

The samples were divided into 4 groups

GROUP I	-	PRIME & BOND NT	(n=20)
GROUP II	-	BEAUTI BOND	(n=20)
GROUP III	-	ADPER EASYONE	(n=20)
GROUP IV	-	XENO V	(n=20)

The four experimental groups were evaluated for degree of conversion for LED and QTH light source. (n=10/light source in each group).

FTIR (Fourier Transform Infra Red) Spectrum Acquisition:

- ✓ KBr (Potassium Bromide) pellet preparation
- ✓ Application of adhesive systems and spectrum acquisition for both light sources.

KBr Pellet Preparation:

a) Sample grinding:

Dried, spectroquality grade KBr is used as the matrix. Approximately 100mg of KBr powder was thoroughly ground in a dry agate mortar and pestle for 3-5 minutes until the resulting powder is like talc.

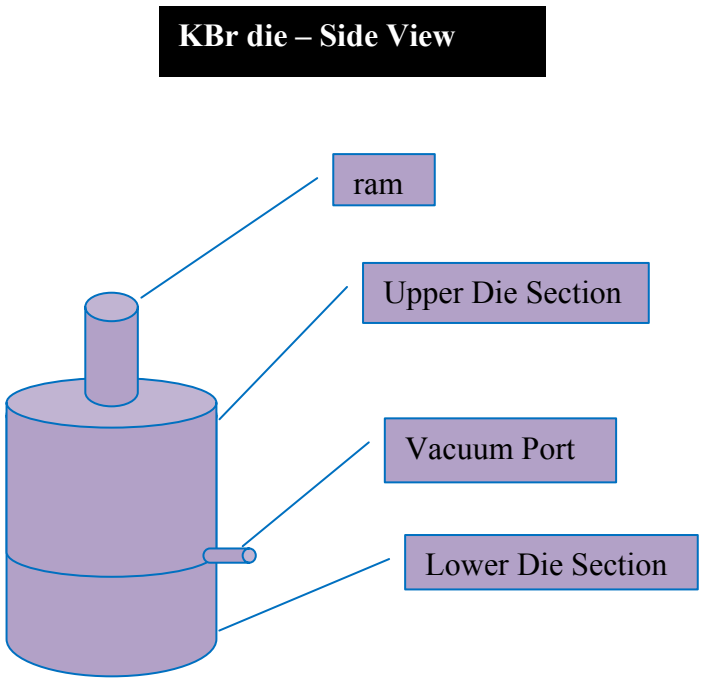


Figure. 1

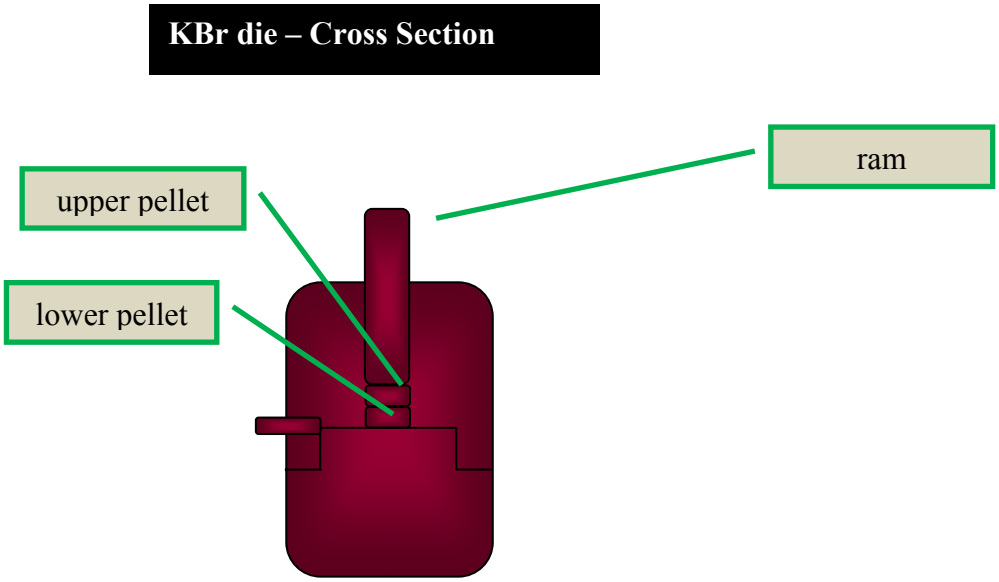


Figure. 2

b) Forming the pellet:

The die parts were wiped clean that will come in contact with the KBr powder. The upper and lower portions of the die were connected and, with the aid of the ram, the lower stainless steel die pellet was pushed into the bore in the top of the die with smooth side up.(Figure 1&2).

The grounded KBr powder was transferred into the bore and the upper stainless steel die pellet was pushed (smooth side down) into the bore. Now the powder was situated between the smooth surfaces of the upper and lower pellets.

The ram was inserted into the bore and the ram pushed down until the ram and pellets are seated at the bottom of the bore. The vacuum hose was connected to the vacuum port and the vacuum pump was turned on . After 10 minutes of evacuation, 8 to 10 tons of pressure applied for 3 to 5 minutes. The screw was tightened on the hydraulic press and repressurizing done. The vacuum pump was shut off and slowly pressure was released from the die by slowly opening the screw.

The die was removed from the hydraulic press. The upper and lower die sections were separated and using tweezers the pressed KBr disk was transferred to the appropriate disk holder for FTIR analysis.

c) Application of adhesive systems and spectrum acquisition for both light sources:

For FTIR analysis of four adhesive systems, a constant volume (0.01ml) of the adhesive resin solution was placed into mixing well using fixed volume micro pipette.

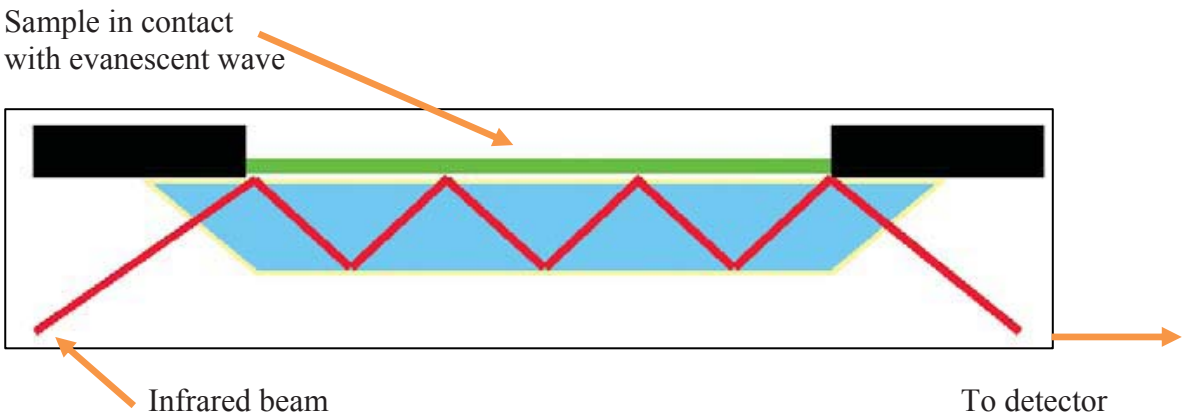


Figure.3

One adhesive layer of constant volume (0.01ml) was applied using an applicator tip on the KBr pellet surface, gently air dried for 5 s and FTIR spectra of non-polymerized adhesive solution were obtained. For each cured sample, the same non cured adhesive sample served as the control. The light was applied on the side opposite the infra red beam scan (Figure.3). The adhesive sample was light-cured for 10 s in both QTH and LED curing units except for BeautiBond which was light cured with LED unit for 5s according to the manufacturer's instructions. Light curing was done with the constant distance of 5mm from the KBr pellet with the help of teflon

tube of 5mm length which was attached to the light guide tip of both QTH and LED light curing units for standardization.

The Perkin Elmer Spectrum1 FTIR instrument consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and mylar beam splitters followed by a sample chamber and detector. In the transmission mode the infrared beam passes the sample and is detected behind the sample. Entire region of 450-4000 cm-1 is covered by this instrument. The interference pattern obtained from a two beam interferometer as the path difference between the two beams is altered, when Fourier transformed, give rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated on-line computer.

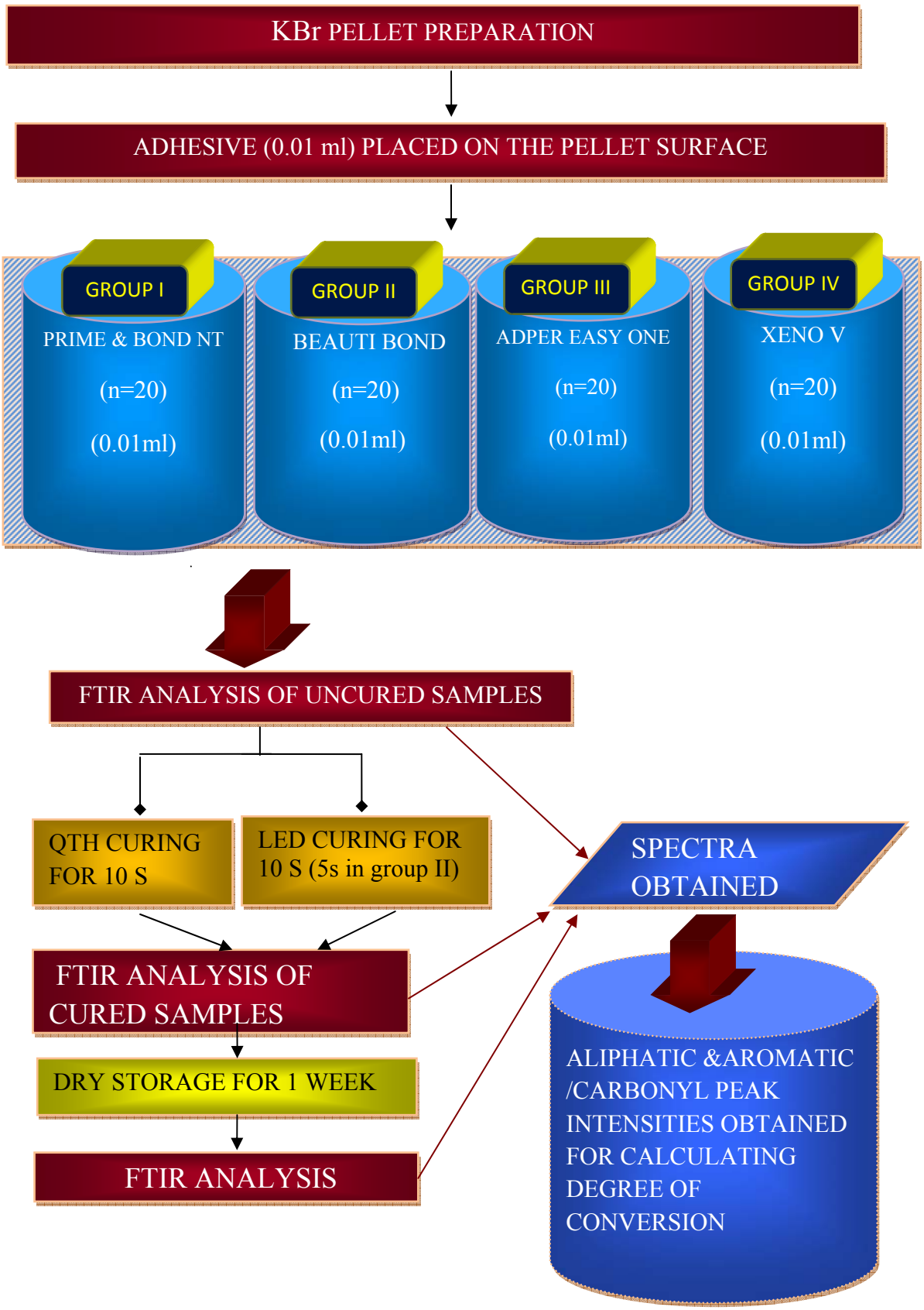
Before each new set of measurements of all the samples, a baseline spectrum was obtained to determine the spectra of the artefacts used in the measurements, which would be deducted by the equipment in the subsequent monomer and polymer measurements of each specimen.

FTIR spectra was obtained using 5 scans at 4 cm^{-1} resolution with the frequency range of 450-4000cm^{-1}in the transmittance mode (PerkinElmer co, Massachusetts, USA) for

1) Non polymerized adhesive solution
2) Immediately after 10-s light curing except for Beauti Bond cured for 5s in LED light source
3) After the sample storage for 1 week

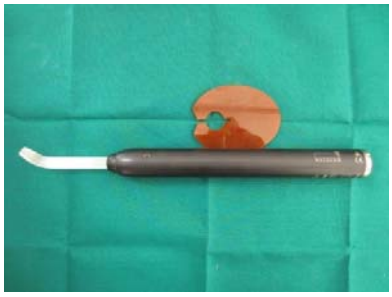
After obtaining the spectra of 10 light cured samples of each material for each light cure unit, the KBr pellets were stored at room temperature to monitor the continuation of polymerization reaction even after 24 hrs.

INVESTIGATION DESIGN:



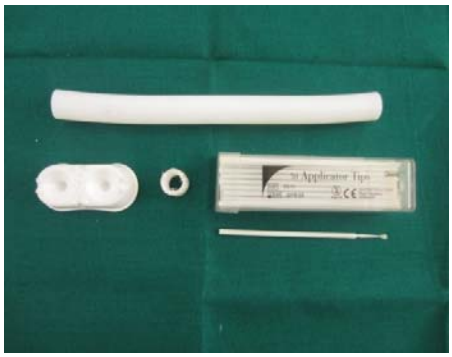
ARMAMENTARIUM

QTH light cure unit

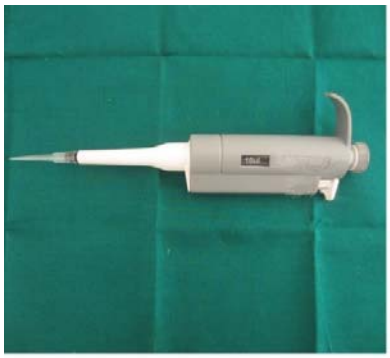


LED light cure unit

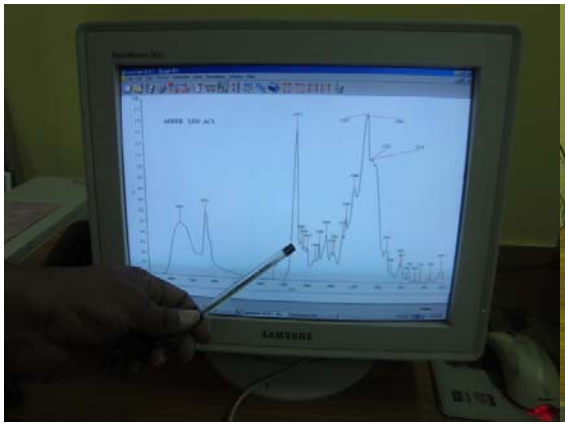
ETCH AND RINSE &ONE STEP SELF ETCH ADHESIVES



Applicator tips& 5mm length Teflon tube

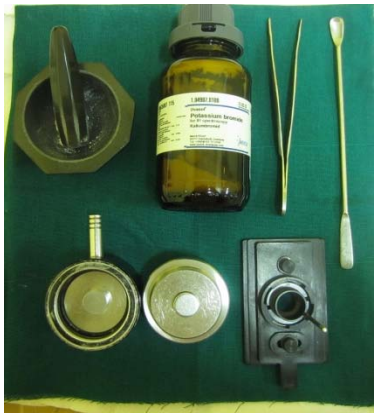


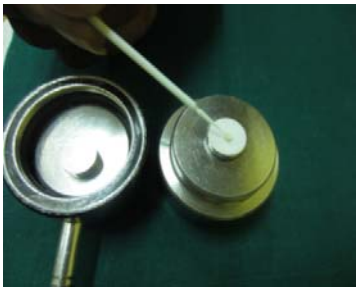
0.01ml micro pipette



Perkin Elmer one spectrum FTIR spectrometer

KBr PELLET PREPARATION





KBr powder pouring into the bore of the die section

Adhesive application on the pellet surface

Prepared KBr pellet

Transferred KBr pellet to the FTIR carrier

Placing the carrier into the FTIR spectrometer

Dry storage

RESULTS

Calculation of conversion:

The Degree Of Conversion (DC) of the adhesive was calculated according to the following formula:

Degree of Conversion = (1 – R cured / R uncured) X 100

Adhesive system	PEAK INTENSITY		
	Aliphatic	Internal standard	
		Aromatic	Carbonyl
Bis GMA based	1639cm-1	1609cm-1	
Non Bis GMA based	1639cm-1		1720cm-1

For Example: Prime & Bond NT (figure.4B)

Aliphatic peak intensity at 1639cm-1 before curing =1.1 A.U

After curing =0.56A.U

Aromatic peak intensity at 1609cm-1 before curing =0.6A.U

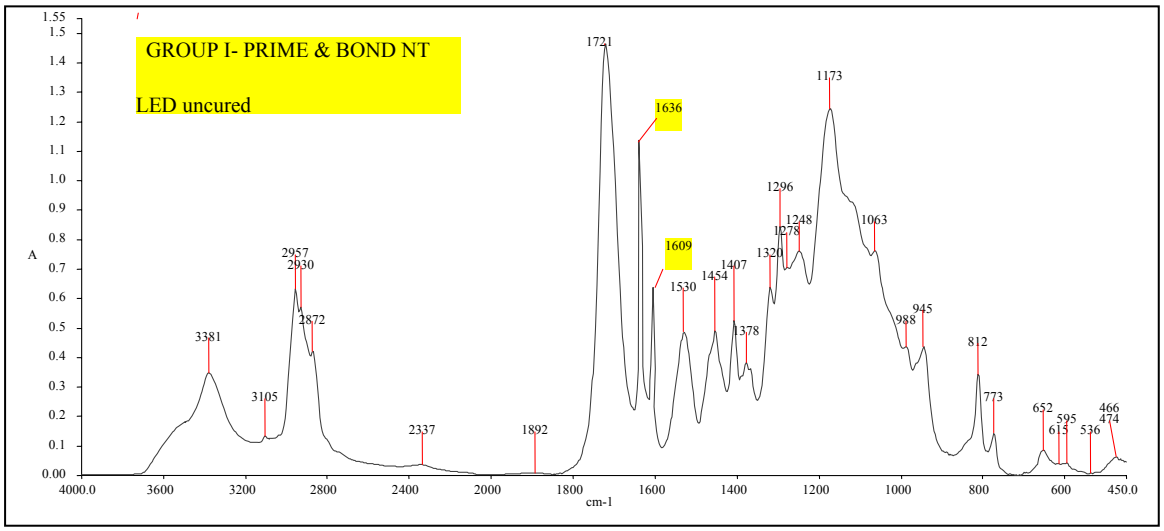
After curing =0.58A.U

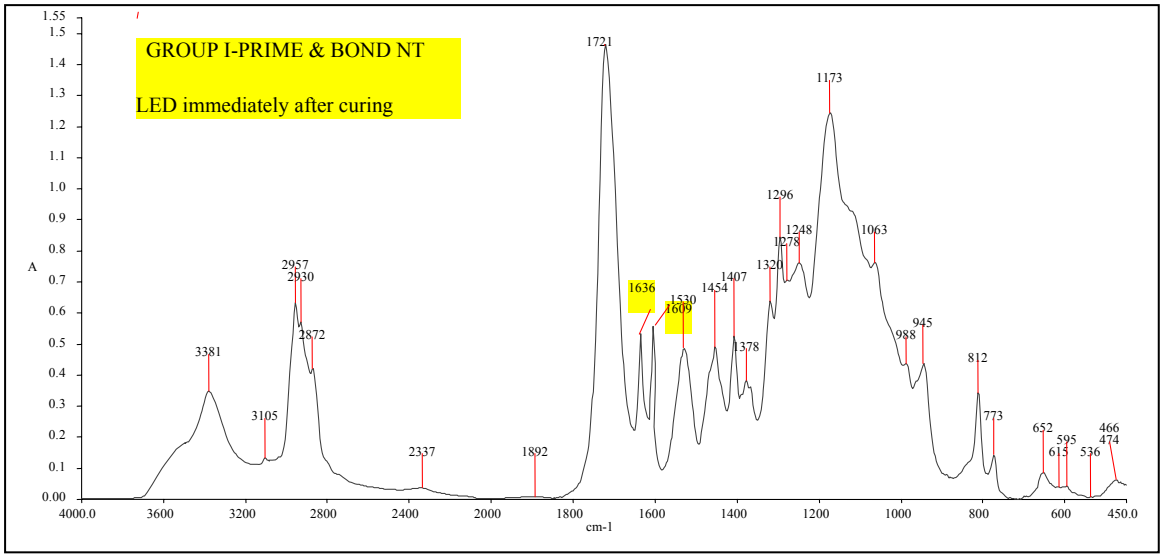
$$\text{Degree of conversion} = 1 - \left(\frac{0.56/0.58}{1.1/0.6} \right) \text{X } 100$$

$$= 1\text{-}0.53 = 0.47 \text{ X } 100 = 47\%$$

The figures 4A, 4B, 5A, 5B, 6A, 6B, 7A & 7B represent a sample spectra with wave number in X axis(cm-1) and arbitrary unit(A.U) in Y axis of each group for which DC was calculated.

FIGURE.4A


GROUP I- PRIME & BOND NT
LED uncured
A
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3381
3105
2957
2930
2872
2337
1892
1721
1636
1609
1530
1454
1407
1378
1320
1296
1278
1248
1173
1063
988
945
812
773
652
615
595
536
474
466


GROUP I-PRIME & BOND NT
LED immediately after curing
A
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3381
3105
2957
2930
2872
2337
1892
1721
1636
1609
1530
1454
1407
1378
1320
1296
1278
1248
1173
1063
988
945
812
773
652
615
595
536
474
466

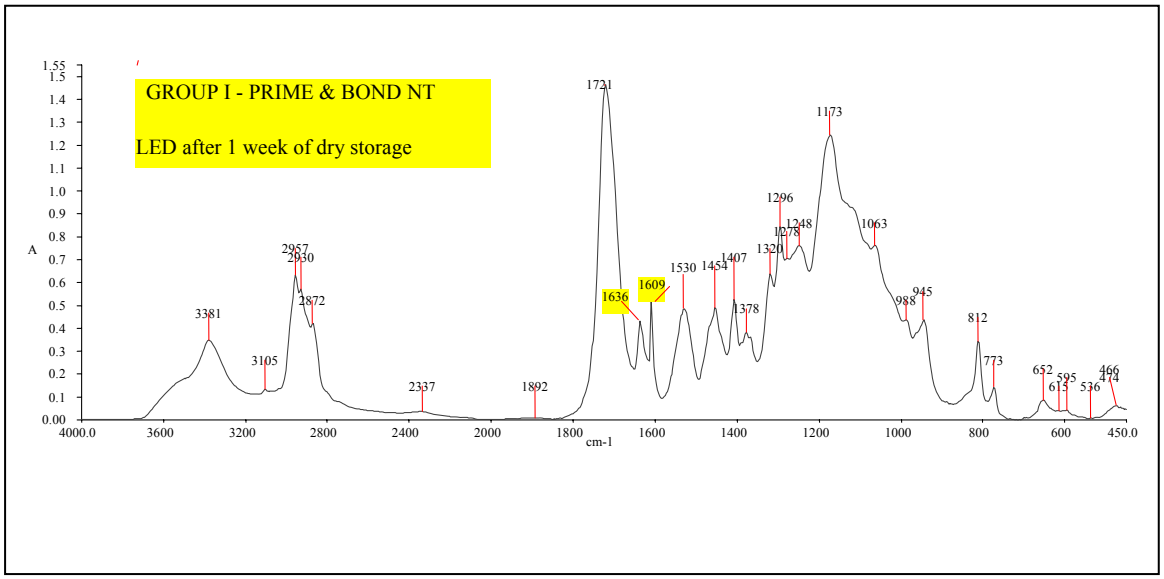
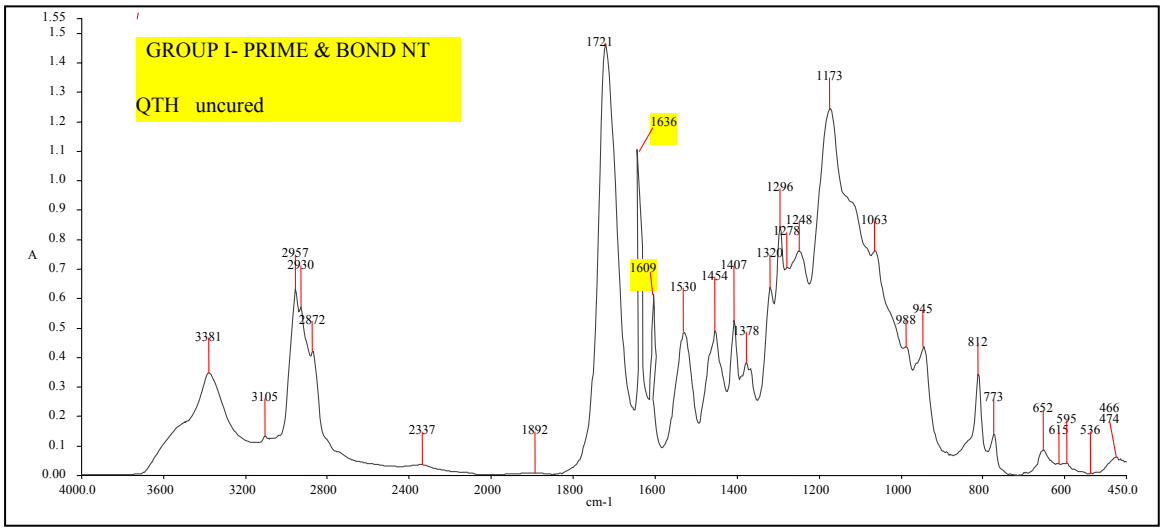
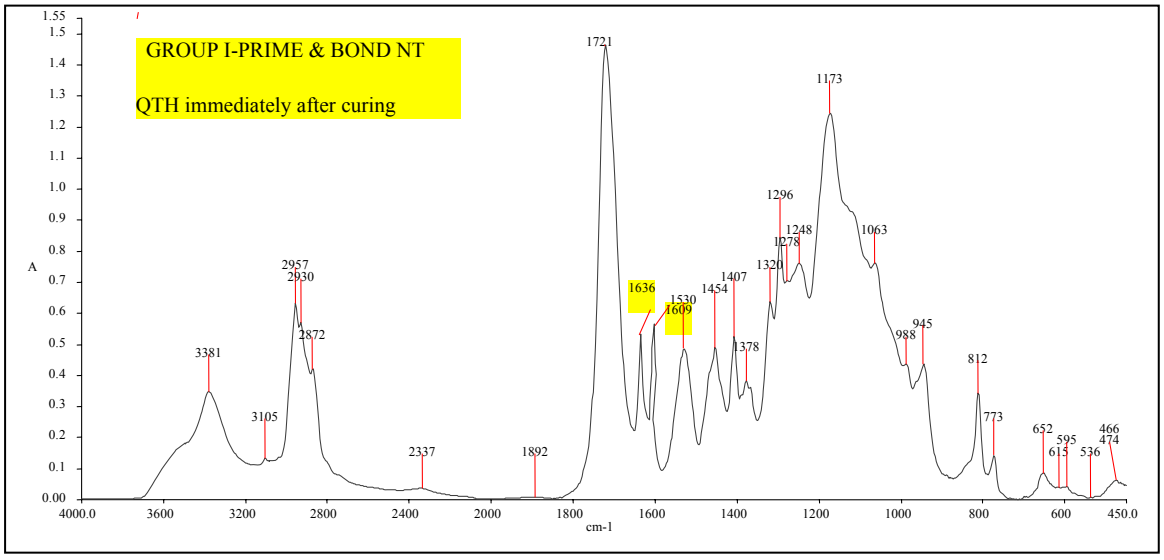

GROUP I - PRIME & BOND NT
LED after 1 week of dry storage
A
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3381
3105
2957
2930
2872
2337
1892
1721
1636
1609
1530
1454
1407
1378
1320
1296
1278
1248
1173
1063
988
945
812
773
652
615
595
536
474
466

FIGURE.4B


GROUP I- PRIME & BOND NT
QTH uncured
A
cm-1
1721
1636
1173
1296
1248
1278
1063
1609
1530
1454
1407
1320
945
988
1378
812
773
652
595
615
536
466
474
2957
2930
2872
3381
3105
2337
1892


GROUP I-PRIME & BOND NT
QTH immediately after curing
A
cm-1
1721
1173
1296
1248
1278
1063
1636
1530
1609
1454
1407
1320
945
988
1378
812
773
652
595
615
536
466
474
2957
2930
2872
3381
3105
2337
1892

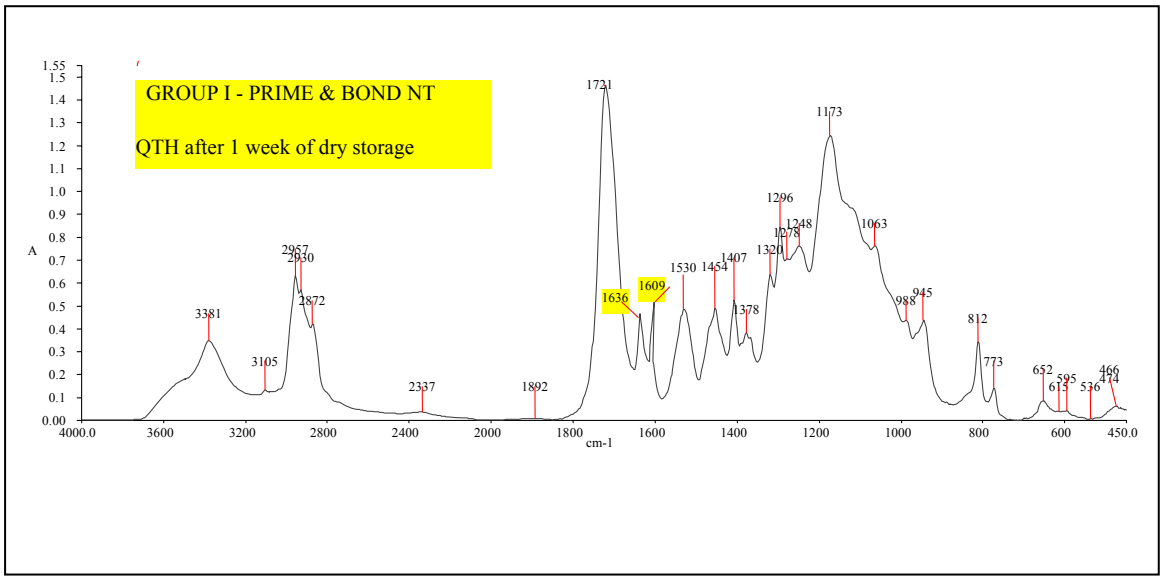
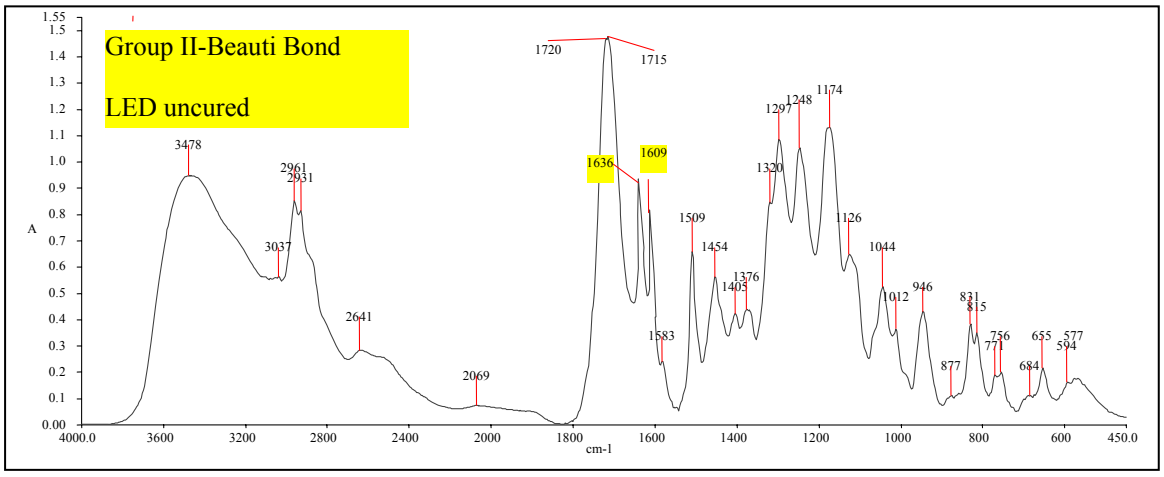
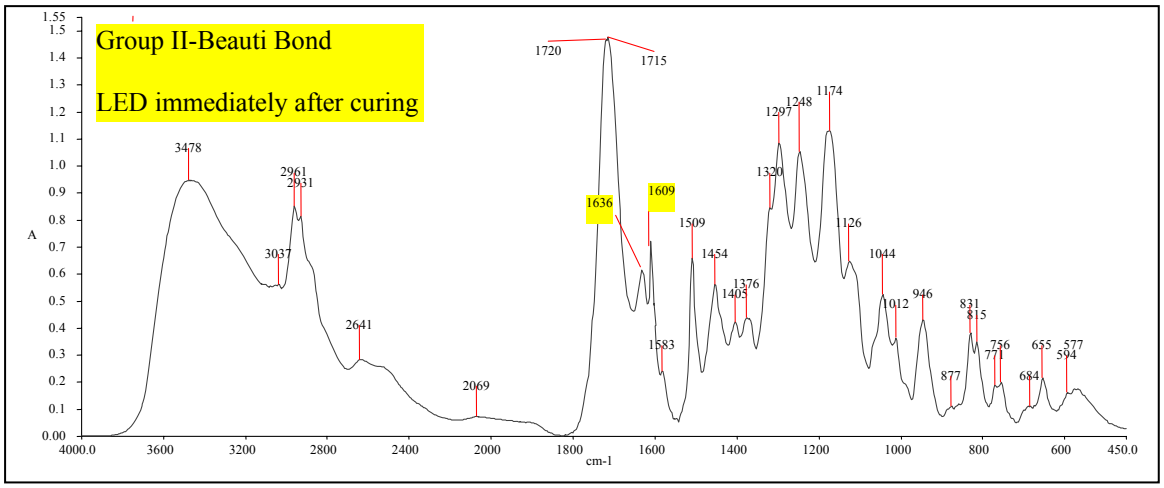

GROUP I - PRIME & BOND NT
QTH after 1 week of dry storage
A
cm-1
1721
1173
1296
1248
1278
1063
1636
1609
1530
1454
1407
1320
945
988
1378
812
773
652
595
615
536
466
474
2957
2930
2872
3381
3105
2337
1892

FIGURE.5A


Group II-Beauti Bond
LED uncured
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1583
1509
1454
1405
1376
1320
1297
1248
1174
1126
1044
1012
946
877
831
815
771
756
684
655
594
577


Group II-Beauti Bond
LED immediately after curing
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1583
1509
1454
1405
1376
1320
1297
1248
1174
1126
1044
1012
946
877
831
815
771
756
684
655
594
577

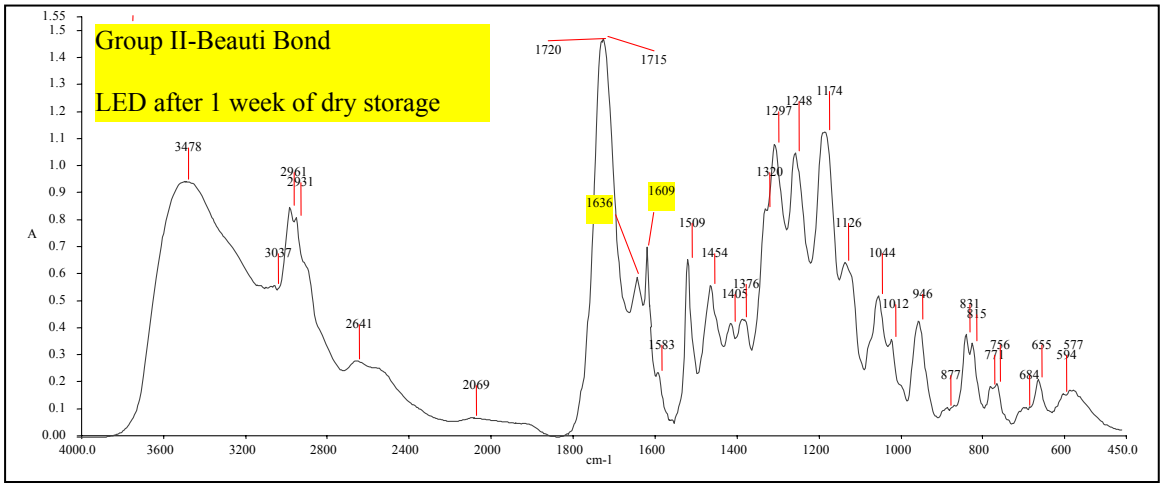
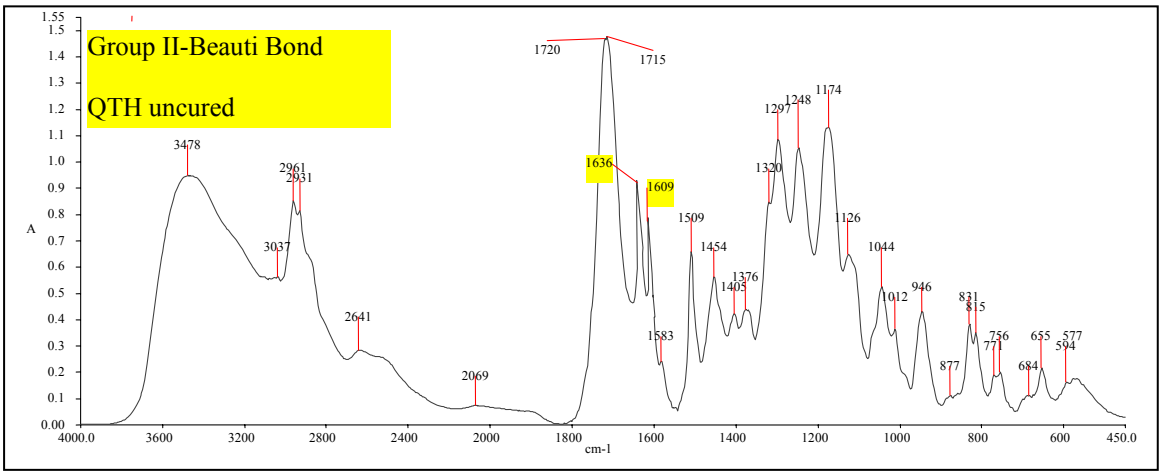
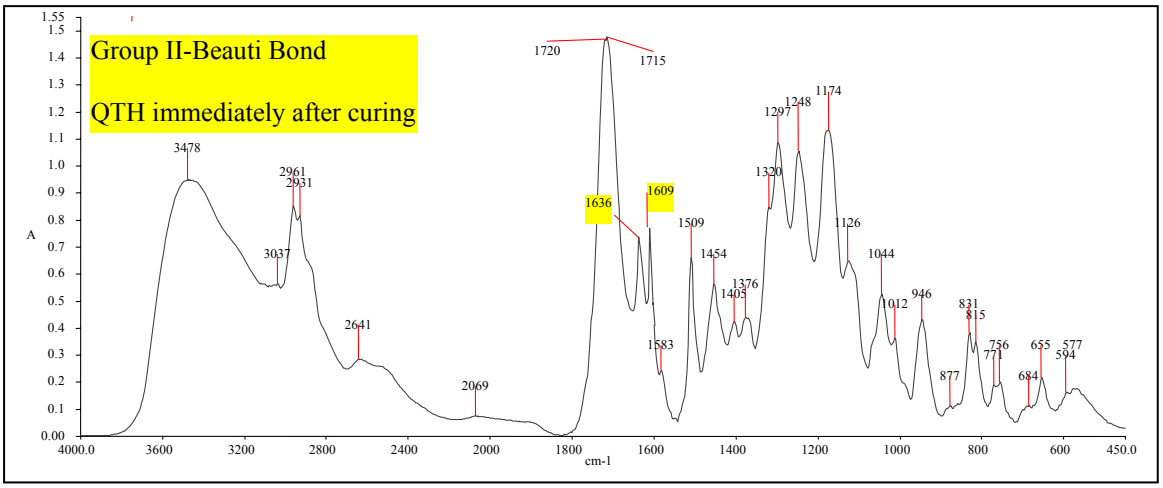

Group II-Beauti Bond
LED after 1 week of dry storage
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1583
1509
1454
1405
1376
1320
1297
1248
1174
1126
1044
1012
946
877
831
815
771
756
684
655
594
577

FIGURE.5B


Group II-Beauti Bond
QTH uncured
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1509
1454
1376
1405
1583
1320
1297
1248
1174
1126
1044
1012
946
831
815
756
771
655
594
577
684
877


Group II-Beauti Bond
QTH immediately after curing
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1509
1454
1376
1405
1583
1320
1297
1248
1174
1126
1044
1012
946
831
815
756
771
655
594
577
684
877

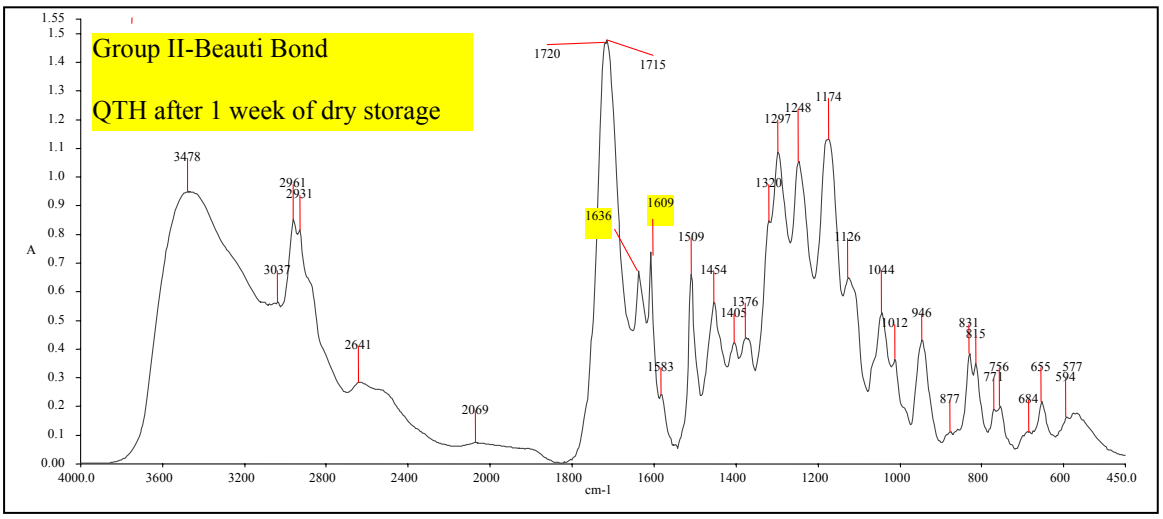
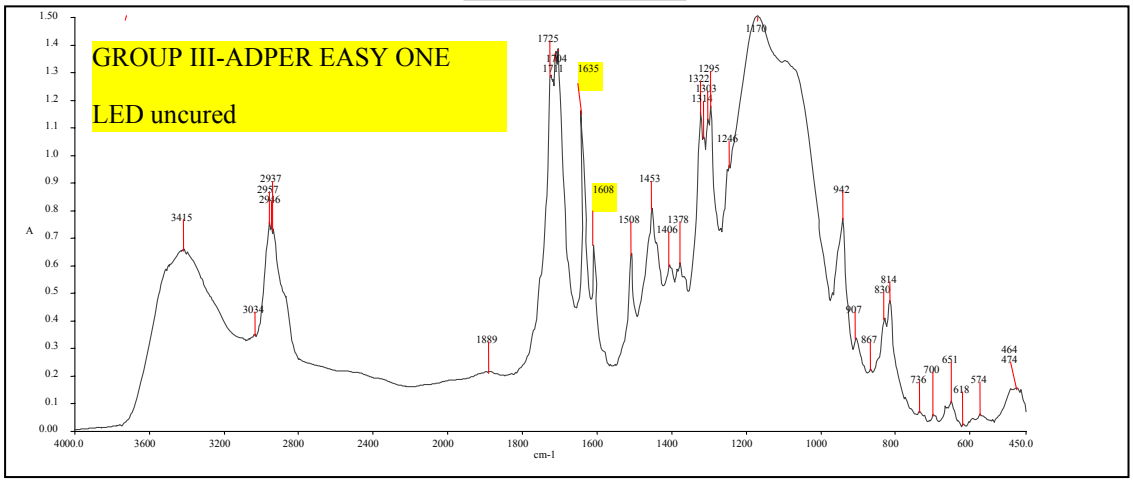
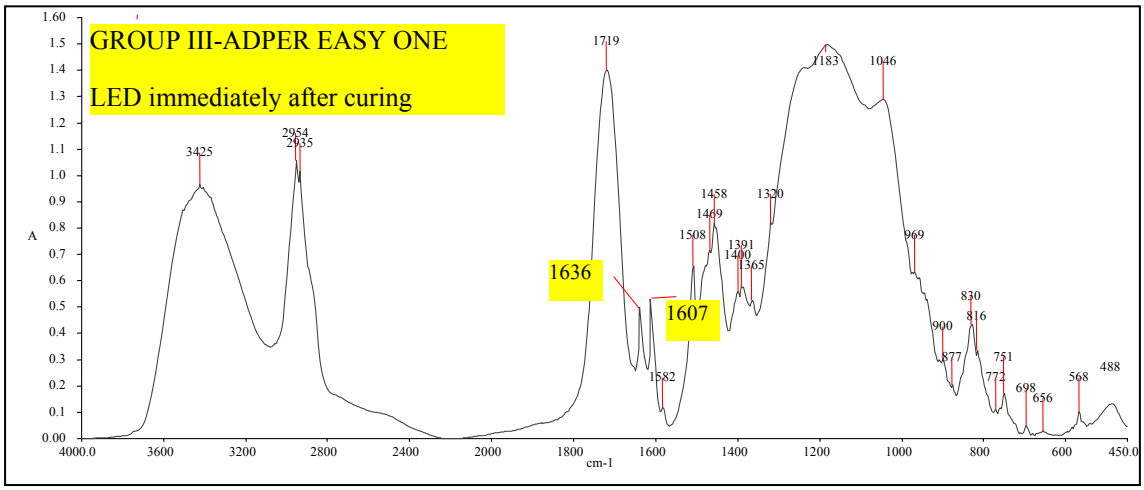

Group II-Beauti Bond
QTH after 1 week of dry storage
A
cm-1
3478
2961
2931
3037
2641
2069
1720
1715
1636
1609
1509
1454
1376
1405
1583
1320
1297
1248
1174
1126
1044
1012
946
831
815
756
771
655
594
577
684
877

FIGURE. 6A


GROUP III-ADPER EASY ONE
LED uncured
A
cm-1


GROUP III-ADPER EASY ONE
LED immediately after curing
1636
1607
A
cm-1

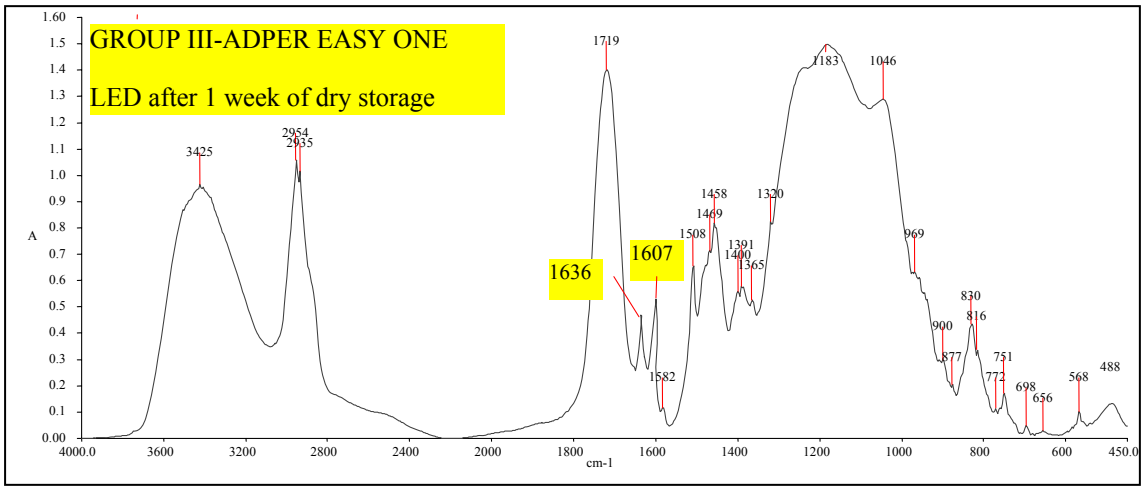
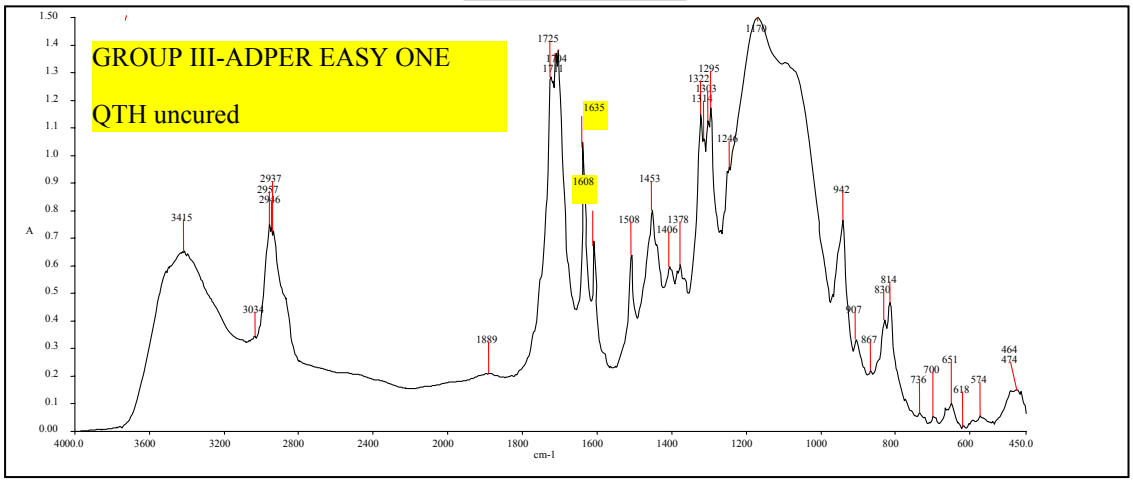
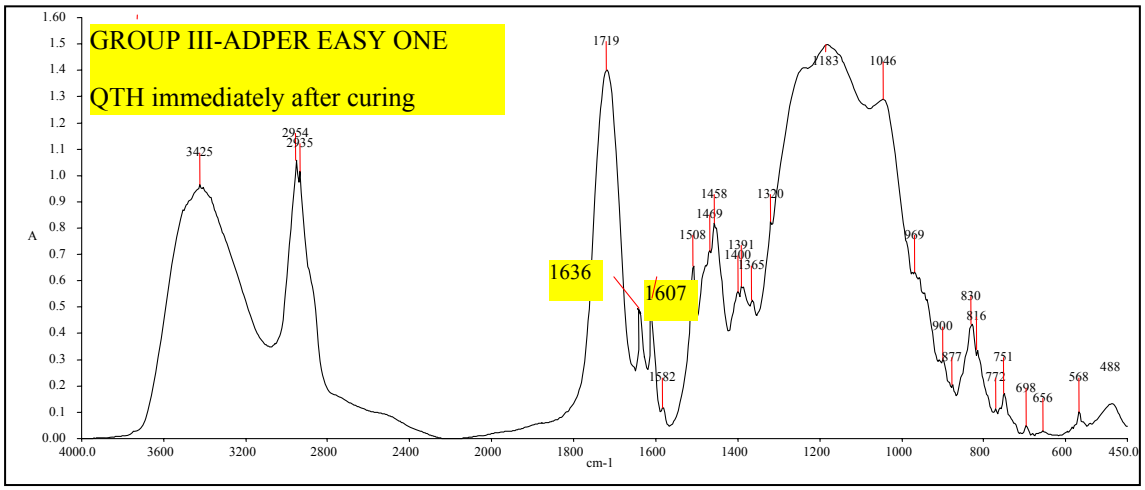

GROUP III-ADPER EASY ONE
LED after 1 week of dry storage
1636
1607
A
cm-1

FIGURE.6B


GROUP III-ADPER EASY ONE
QTH uncured
3415
2937
2957
2906
3034
1889
1725
1714
1701
1635
1608
1508
1453
1406
1378
1322
1303
1295
1246
1179
942
907
867
814
830
736
700
651
618
574
464
474
A
cm-1


GROUP III-ADPER EASY ONE
QTH immediately after curing
3425
2954
2935
1719
1636
1607
1582
1508
1469
1458
1400
1391
1365
1320
1183
1046
969
900
877
830
816
772
751
698
656
568
488
A
cm-1

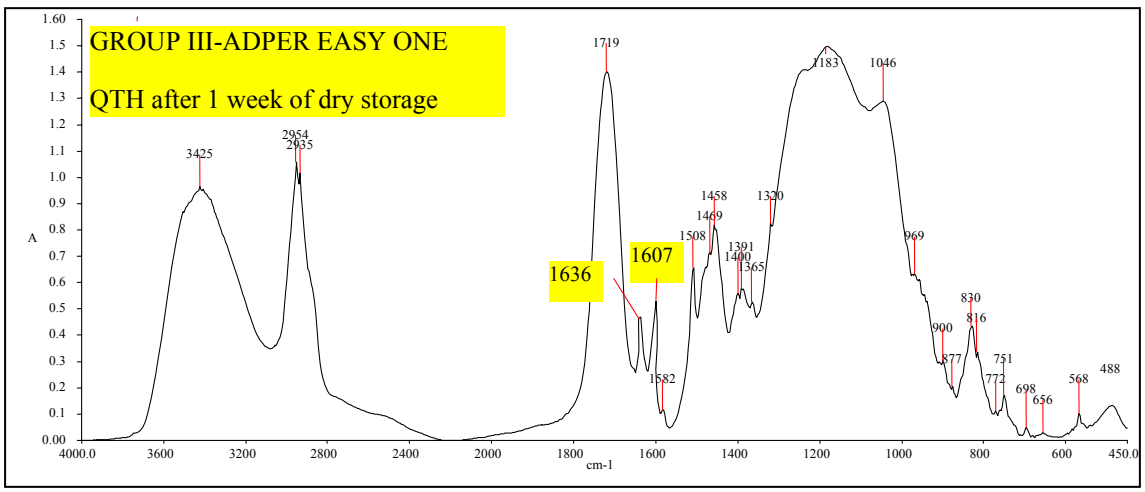
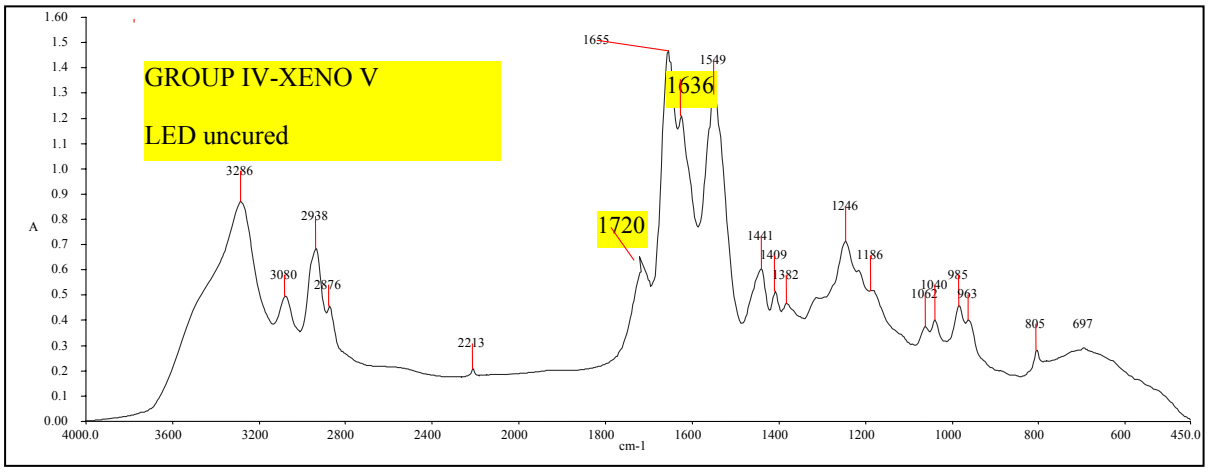
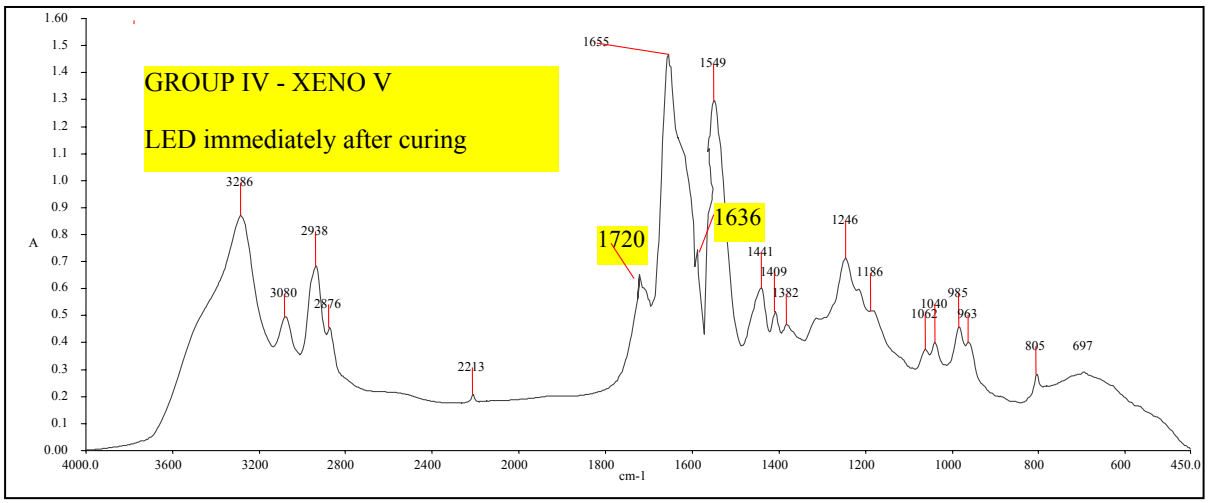

GROUP III-ADPER EASY ONE
QTH after 1 week of dry storage
3425
2954
2935
1719
1636
1607
1582
1508
1469
1458
1400
1391
1365
1320
1183
1046
969
900
877
830
816
772
751
698
656
568
488
A
cm-1

FIGURE.7A


GROUP IV-XENO V
LED uncured
1655
1549
1636
3286
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
2213
805
697
A
cm-1


GROUP IV - XENO V
LED immediately after curing
1655
1549
3286
1636
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
2213
805
697
A
cm-1

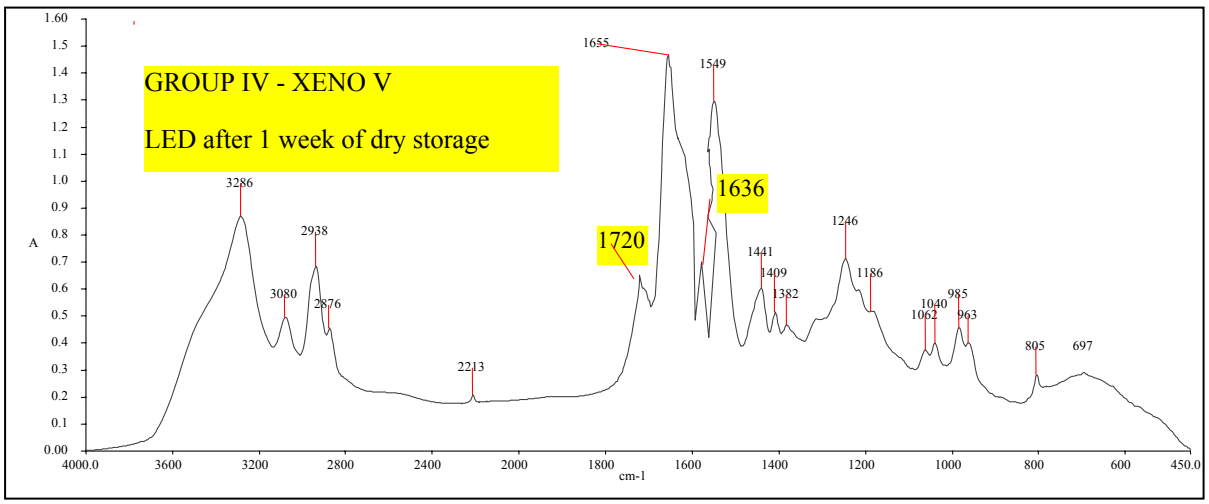
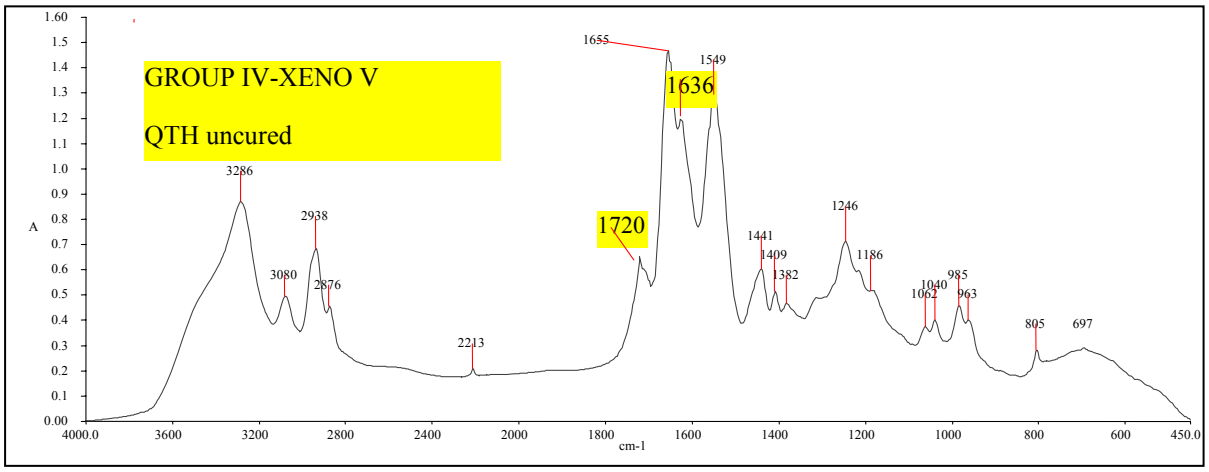
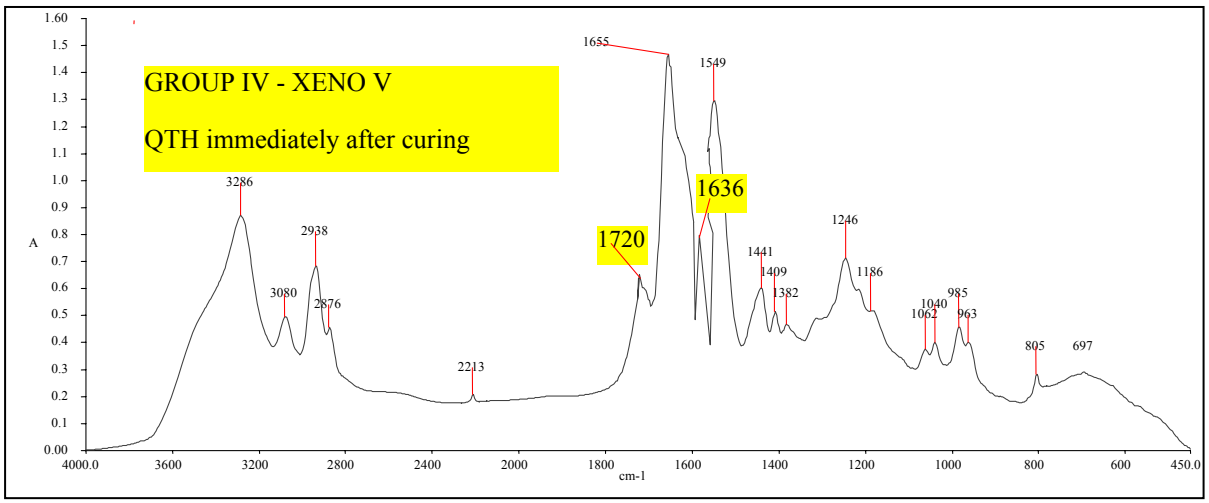
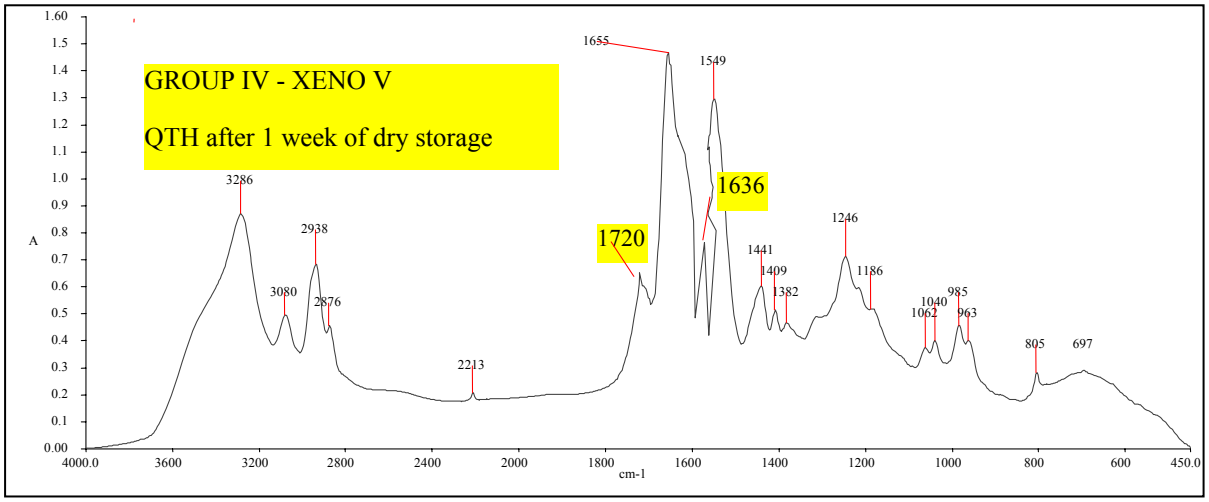

GROUP IV - XENO V
LED after 1 week of dry storage
1655
1549
3286
1636
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
2213
805
697
A
cm-1

FIGURE.7B


GROUP IV-XENO V
QTH uncured
1655
1549
1636
3286
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
805
697
2213
A
cm-1


GROUP IV - XENO V
QTH immediately after curing
1655
1549
1636
3286
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
805
697
2213
A
cm-1


GROUP IV - XENO V
QTH after 1 week of dry storage
1655
1549
1636
3286
2938
1720
1246
1441
1409
1186
3080
2876
1382
1040
1062
985
963
805
697
2213
A
cm-1

RESULTS:

TABLE I: DC of group I (Prime & Bond NT) immediately after curing and after 1 week of dry storage

BONDING AGENT GROUP I PRIME&BOND NT	DEGREE OF CONVERSION IMMEDIATELY AFTER CURING		DEGREE OF CONVERSION AFTER 1 WEEK OF DRY STORAGE	
	QTH	**LED**	**QTH**	**LED**
1.	42	45.8	49.8	51.2
2.	45	47.2	50	55.8
3.	47	48.5	52.8	58
4.	38.85	51	43.2	56.3
5.	36.2	53.2	45.85	59
6.	40.5	55.4	49	59
7.	39.5	53	46.3	60.2
8.	42.5	49	49	55.8
9.	44.2	50.8	48.6	56.4
10.	45.85	51	50.2	59

TABLE II: DC of group II (Beauti Bond) immediately after curing and after 1 week of dry storage

BONDING AGENT GROUP II BEAUTI BOND	DEGREE OF CONVERSION IMMEDIATELY AFTER CURING		DEGREE OF CONVERSION AFTER 1 WEEK OF DRY STORAGE	
	QTH	**LED**	**QTH**	**LED**
1.	22	31	29	38.3
2.	24	29.5	28.85	37
3.	25.8	29	26	35.2
4.	29	32	32.8	36.2
5.	27.5	31.5	32.8	37.85
6.	31	30.5	35.2	39.8
7.	24.85	29.8	30	36.85
8.	26.2	29.85	31.2	39
9.	23.8	31.5	30.85	37
10.	27	32.2	30.3	39

TABLE III: DC of group III (Adper Easy One) immediately after curing and after 1 week of dry storage

BONDING AGENT GROUP III ADPER EASY ONE	DEGREE OF CONVERSION IMMEDIATELY AFTER CURING		DEGREE OF CONVERSION AFTER 1 WEEK OF DRY STORAGE	
	QTH	LED	QTH	LED
1.	46.5	51	50.85	54
2.	47	49.5	51.3	55.6
3.	44	52.2	47.6	58
4.	46.5	49.5	49.5	54
5.	42	50.85	47.6	54.2
6.	45.5	49.2	50	55.8
7.	47	51.5	50.5	55.8
8.	43.5	50.8	49.85	57
9.	42.2	53	49	58.2
10.	42	50.85	49	58.2

TABLE IV: DC of group IV (Xeno V) immediately after curing and after 1 week of dry storage

BONDING AGENT GROUP IV XENO V	DEGREE OF CONVERSION IMMEDIATELY AFTER CURING		DEGREE OF CONVERSION AFTER 1 WEEK OF DRY STORAGE	
	QTH	LED	QTH	LED
1.	55.85	59	60.5	65.8
2.	58	62.4	61	64.3
3.	54.2	58	62.2	65.8
4.	54.2	61	59.85	63.6
5.	56	60.8	59	63.6
6.	56	62	61	67.4
7.	53	61.4	60.85	66
8.	55.85	59.85	59	62.8
9.	53	60.6	60.85	64
10.	54	61.85	59.5	65.8

STATISTICAL ANALYSIS:

Data were statistically analyzed using ONE WAY ANOVA and TUKEY'S HSD Post-hoc multiple comparisons and paired t test at 1% level significance.

TABLE V:

Groups	**DC immediately after curing**				**DC after 1 week of dry storage**			
	QTH		**LED**		**QTH**		**LED**	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Group I	42.16[b]	3.43	50.49[b]	2.93	48.48[b]	2.70	57.07[b]	2.59
Group II	26.12[a]	2.65	30.68[a]	1.12	30.70[a]	2.55	37.62[a]	1.43
Group III	44.62[b]	2.12	50.84[b]	1.21	49.52[b]	1.25	56.08[b]	1.70
Group IV	55.01[c]	1.59	60.69[c]	1.39	60.38[c]	1.02	64.91[c]	1.45
P value	<0.001**		<0.001**		<0.001**		<0.001**	

1) ** denotes significance at 1% level

2) Means followed by different alphabets between groups denotes significance at 1% level using TUKEY'S HSD Post-hoc test.

TABLE VI:

Dependent Variable	**(I) Group**	**(J) Group**	**Mean Difference (I-J)**	**Std. Error**	**Sig.**	**95% Confidence Interval**	
						Lower Bound	**Upper Bound**
QTH after curing	Group I	Group II	16.0450(*)	1.13578	.000	12.9861	19.1039
		Group III	-2.4600	1.13578	.152	-5.5189	.5989
		Group IV	-12.8500(*)	1.13578	.000	-15.9089	-9.7911
	Group II	Group I	-16.0450(*)	1.13578	.000	-19.1039	-12.9861
		Group III	-18.5050(*)	1.13578	.000	-21.5639	-15.4461

		Group IV	-28.8950(*)	1.13578	.000	-31.9539	-25.8361
	Group III	Group I	2.4600	1.13578	.152	-.5989	5.5189
		Group II	18.5050(*)	1.13578	.000	15.4461	21.5639
		Group IV	-10.3900(*)	1.13578	.000	-13.4489	-7.3311
	Group IV	Group I	12.8500(*)	1.13578	.000	9.7911	15.9089
		Group II	28.8950(*)	1.13578	.000	25.8361	31.9539
		Group III	10.3900(*)	1.13578	.000	7.3311	13.4489
LED after curing	Group I	Group II	19.8050(*)	.81391	.000	17.6129	21.9971
		Group III	-.3500	.81391	.973	-2.5421	1.8421
		Group IV	-10.2000(*)	.81391	.000	-12.3921	-8.0079
	Group II	Group I	-19.8050(*)	.81391	.000	-21.9971	-17.6129
		Group III	-20.1550(*)	.81391	.000	-22.3471	-17.9629
		Group IV	-30.0050(*)	.81391	.000	-32.1971	-27.8129
	Group III	Group I	.3500	.81391	.973	-1.8421	2.5421
		Group II	20.1550(*)	.81391	.000	17.9629	22.3471
		Group IV	-9.8500(*)	.81391	.000	-12.0421	-7.6579
	Group IV	Group I	10.2000(*)	.81391	.000	8.0079	12.3921
		Group II	30.0050(*)	.81391	.000	27.8129	32.1971
		Group III	9.8500(*)	.81391	.000	7.6579	12.0421
QTH after 1 week	Group I	Group II	17.7750(*)	.90592	.000	15.3352	20.2148
		Group III	-1.0450	.90592	.659	-3.4848	1.3948
		Group	-11.9000(*)	.90592	.000	-	-9.4602

		IV				14.3398	
	Group II	Group I	-17.7750(*)	.90592	.000	-20.2148	-15.3352
		Group III	-18.8200(*)	.90592	.000	-21.2598	-16.3802
		Group IV	-29.6750(*)	.90592	.000	-32.1148	-27.2352
	Group III	Group I	1.0450	.90592	.659	-1.3948	3.4848
		Group II	18.8200(*)	.90592	.000	16.3802	21.2598
		Group IV	-10.8550(*)	.90592	.000	-13.2948	-8.4152
	Group IV	Group I	11.9000(*)	.90592	.000	9.4602	14.3398
		Group II	29.6750(*)	.90592	.000	27.2352	32.1148
		Group III	10.8550(*)	.90592	.000	8.4152	13.2948
LED after 1 week	Group I	Group II	19.4500(*)	.82938	.000	17.2163	21.6837
		Group III	.9900	.82938	.635	-1.2437	3.2237
		Group IV	-7.8400(*)	.82938	.000	-10.0737	-5.6063
	Group II	Group I	-19.4500(*)	.82938	.000	-21.6837	-17.2163
		Group III	-18.4600(*)	.82938	.000	-20.6937	-16.2263
		Group IV	-27.2900(*)	.82938	.000	-29.5237	-25.0563
	Group III	Group I	-.9900	.82938	.635	-3.2237	1.2437
		Group II	18.4600(*)	.82938	.000	16.2263	20.6937
		Group IV	-8.8300(*)	.82938	.000	-11.0637	-6.5963
	Group IV	Group I	7.8400(*)	.82938	.000	5.6063	10.0737
		Group II	27.2900(*)	.82938	.000	25.0563	29.5237
		Group III	8.8300(*)	.82938	.000	6.5963	11.0637

I.INTERPRETATION OF RESULTS: (Table V & VI)

The results for Degree of conversion (DC) of the factors "bonding agent"($p<0.001$) and "Light cure unit"($p<0.001$) were significant as well as their interaction($p<0.001$).

A) Immediately after curing with LED/QTH light units:

Analysis of the results of DC at 1% level significance reveals that

Group IV (Xeno V) > Group III (Adper Easy One) ≥ Group I (Prime & Bond NT) > Group II (Beauti Bond)

The results of this study showed that the DC of group I (Prime&Bond NT) showed statistically significant difference with group II (Beauti Bond) and group IV (Xeno V) ($p<0.001$) and no statistically significant difference was seen with group III (Adper Easy One). ($p<0.001$)

B) Post polymerization curing after 1 week of dry storage with LED unit

Group IV > Group I ≥ Group III > Group II

The results showed that the DC of group I (Prime&Bond NT) showed statistically significant difference with group II (Beauti Bond) and group IV (Xeno V) ($p<0.001$) and no statistically significant difference was seen with group III (Adper Easy One). ($p<0.001$)

C) Post polymerization curing after 1 week of dry storage with QTH unit

Group IV > Group III ≥ Group I > Group II

The results showed that the DC of group I (Prime & Bond NT) showed statistically significant difference with group II (Beauti Bond) and group IV (Xeno V) ($p<0.001$) and no statistically significant difference was seen with group III (Adper Easy One). ($p<0.001$)

t test:

PAIRED SAMPLES STATISTICS:

Table VII: FOR GROUP I

		Mean	N	Std. Deviation	P value
Pair 1	QTH after curing	42.1600	10	3.42732	<0.001*
	LED after curing	50.4900	10	2.93199	
Pair 2	QTH after 1 week	48.4750	10	2.70342	<0.001*
	LED after 1 week	57.0700	10	2.59403	
Pair 3	QTH after curing	42.1600	10	3.42732	<0.001*
	QTH after 1 week	48.4750	10	2.70342	
Pair 4	LED after curing	50.4900	10	2.93199	<0.001*
	LED after 1 week	57.0700	10	2.59403	

*denotes significance at 1% level

TABLE VIII: FOR GROUP II

		Mean	N	Std. Deviation	P value
Pair 1	QTH after curing	26.1150	10	2.65331	<0.001*
	LED after curing	30.6850	10	1.11606	
Pair 2	QTH after 1 week	30.7000	10	2.54722	<0.001*
	LED after 1 week	37.6200	10	1.42638	
Pair 3	QTH after curing	26.1150	10	2.65331	<0.001*
	QTH after 1 week	30.7000	10	2.54722	
Pair 4	LED after curing	30.6850	10	1.11606	<0.001*
	LED after 1 week	37.6200	10	1.42638	

TABLE IX: FOR GROUPIII

		Mean	N	Std. Deviation	P value
Pair 1	QTH after curing	44.6200	10	2.11859	<0.001*
	LED after curing	50.8400	10	1.21376	
Pair 2	QTH after 1 week	49.5200	10	1.25393	<0.001*
	LED after 1 week	56.0800	10	1.70281	
Pair 3	QTH after curing	44.6200	10	2.11859	<0.001*
	QTH after 1 week	49.5200	10	1.25393	
Pair 4	LED after curing	50.8400	10	1.21376	<0.001*
	LED after 1 week	56.0800	10	1.70281	

TABLE X: FOR GROUP IV

		Mean	N	Std. Deviation	P value
Pair 1	QTH after curing	55.0100	10	1.58899	<0.001*
	LED after curing	60.6900	10	1.39060	
Pair 2	QTH after 1 week	60.3750	10	1.02205	<0.001*
	LED after 1 week	64.9100	10	1.44718	
Pair 3	QTH after curing	55.0100	10	1.58899	<0.001*
	QTH after 1 week	60.3750	10	1.02205	
Pair 4	LED after curing	60.6900	10	1.39060	<0.001*
	LED after 1 week	64.9100	10	1.44718	

II.INTERPRETATION OF TABLE (VII,VIII, IX, X)

A. Comparison of DC with LED and QTH unit

LED UNIT > QTH UNIT

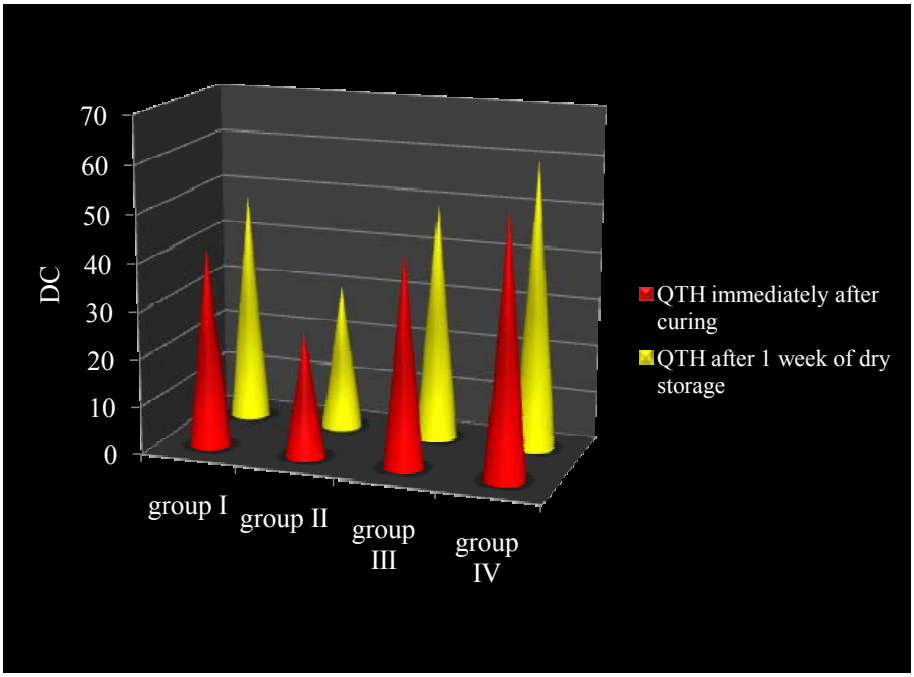
The results showed that the DC when cured with LED unit in Group I (Prime&Bond NT) , Group II (Beauti Bond) , Group III (Adper Easy One) and Group IV (Xeno V) showed statistically significant difference ($p<0.001$) with QTH unit DC.

B. Comparison of DC with immediately after curing and after 1 week of dry storage:

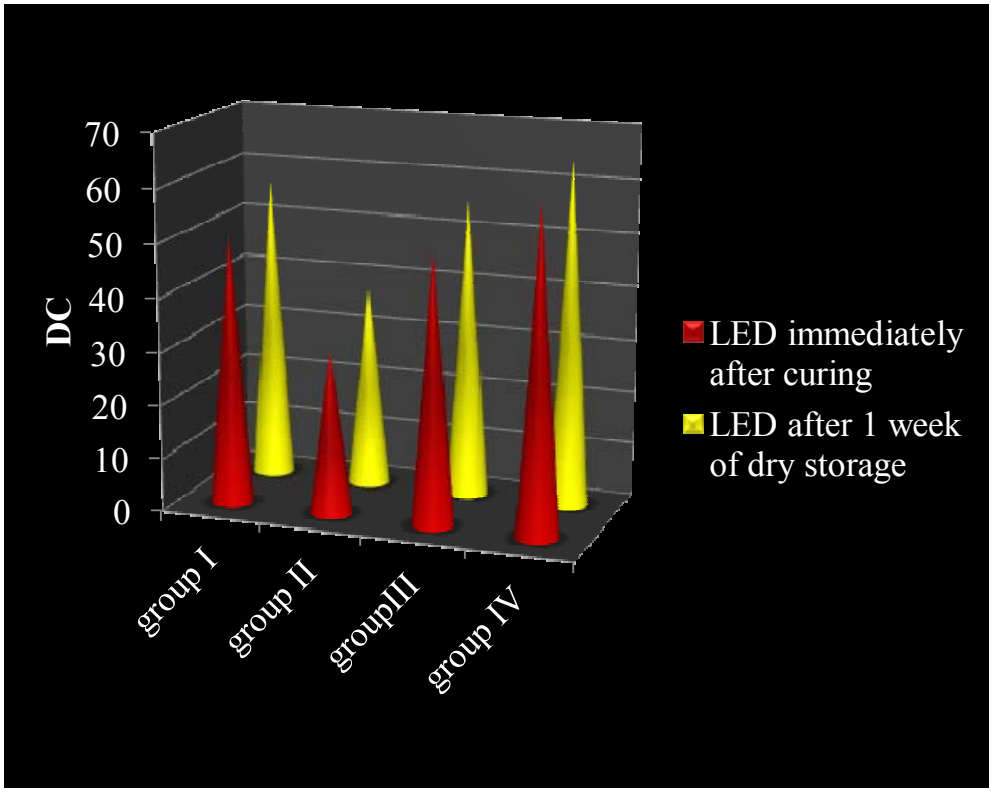
DC after 1 week of dry storage > DC immediately after curing

In all the four groups(Prime & Bond NT, Beauti Bond, Adper Easy One, and Xeno V) the DC after 1 week of dry storage showed statistically significant difference with immediately after curing in both LED and QTH curing unit. ($P < 0.001$)

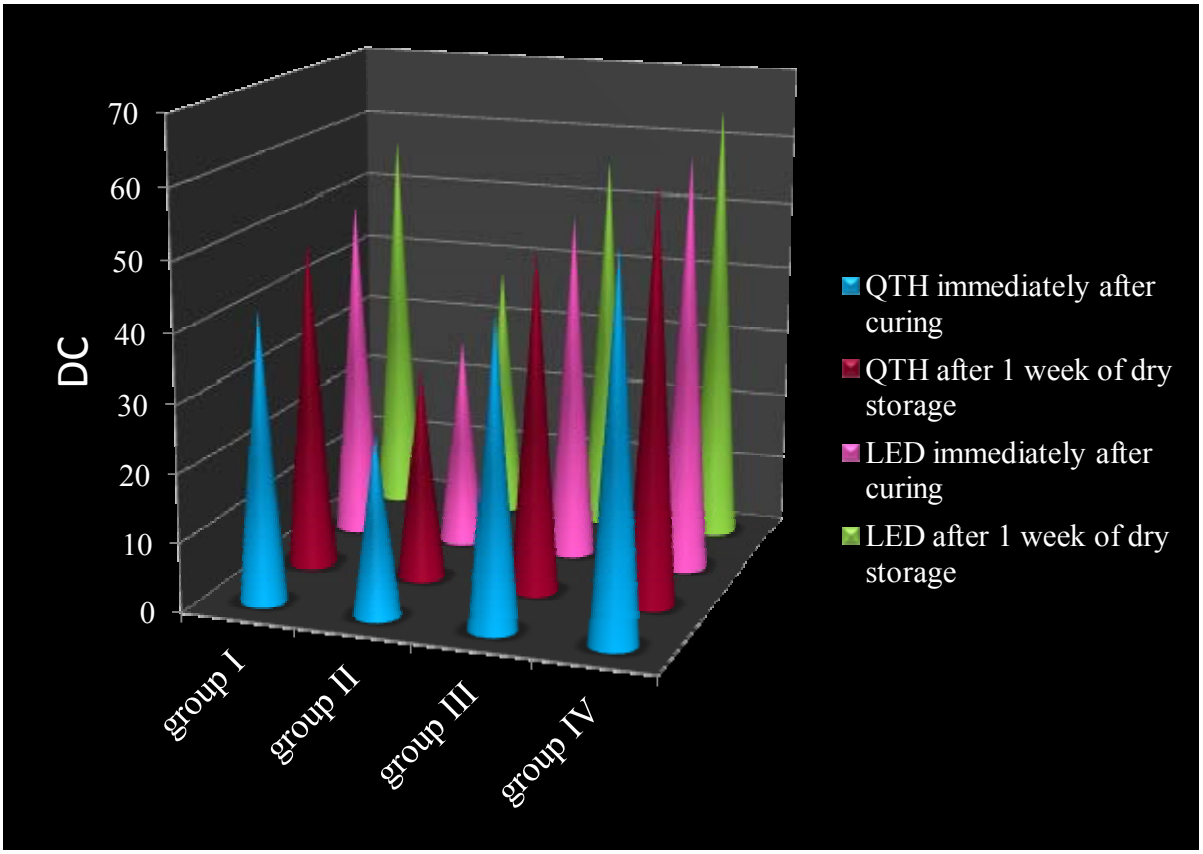
GRAPH I: DC for QTH unit immediately and after 1 week of dry storage



GRAPH II: DC for LED unit immediately and after 1 week of dry storage



GRAPH III: DC FOR LED AND QTH LIGHT CURING UNIT



DISCUSSION

There has been a general trend to simplify the clinical procedures since the beginning of adhesive dentistry. The most common approach was to shorten the time of the adhesive system's application and to reduce the number of steps that lead to the development of one step self-etch adhesive systems. The new generation high power LED curing units are transcending the use of conventional QTH curing units. There has been a significant improvement in the present day adhesive performance that allow the adhesive restorations with a high predictable level of clinical success. When Kanca[44] introduced the concept of "wet-bonding", the strength of resin–dentin bonds increased that allows good sealing of dentin and much less post-operative pain. The resin–dentin bonds equalled or exceeded resin–enamel bonds that lead to the era of safe, reproducible resin–dentin bonding with the revolution of the newer generation of bonding agents. In the self-etch adhesives, the acid base resistant zone is formed which is mechanically, biologically and chemically more resistant than normal dentin, referred as "super dentin", which prevents secondary caries.[60]

In the present study, Prime & Bond NT is the control group. Over a decade, Prime & Bond NT, a two-step etch-and-rinse adhesive has been advocated which contributes a proven clinical longevity with sufficient bond strength. The three commercially available (Beauti Bond,Adper Easy One,and Xeno V) one-step self-etch adhesives were chosen and its degree of conversion was compared with Prime & Bond NT. Among the one-step self-etch adhesives, Beautibond is BisGMA based and it is unique with its HEMA free composition. Adper Easy one adhesive is BisGMA based and

has ethanol solvent and added a new coinitiator TPO whereas in Xeno V which is non BisGMA based and has coinitiator butylated benzene. The Prime & Bond NT & XenoV come from the same manufacturer (Dentsply). By using the adhesive systems from the same manufacturer, certain chemical variations got rid of, allowing a controlled evaluation of the advancement from etch-and-rinse adhesives via two-step to one-step self-etch systems. So, these three adhesives which show differences in their functional monomers, organic solvent and initiator, were chosen and compared with Prime & Bond NT.

Compared to conventional QTH curing units, LED curing units have a narrower wavelength spectrum in the range of 440-490 nm, close to the efficient wavelength for activation of camphorquinone. The LED curing units have diodes that have a life-time of more than 10,000 hours and as in QTH there is no degrading of bulb, reflector or filter over time which results in reduction of curing effectiveness. In newer generations of LEDs, the presence of large surface emitting LED chips provides the power densities up to 900 mW/cm2[16]. The energy efficiency (the relation between power input and light output) of LED is 13% and for QTH it is only 0.7%[29]. The absence of fan and its energy efficiency make the LED unit as less energy consuming one compared to QTH.

The degree of conversion of resins is the main factor influencing the bulk physical properties. The greater mechanical strength was obtained by higher conversion of double bonds. The sub optimal polymerization cause the leaching of the unreacted monomer from the polymerized material and irritate the soft tissue. Moreover, monomer trapped in the restoration may reduce the clinical serviceability of the restoration via oxidation and

hydrolytic degradation, that could be manifested in forms such as discoloration and accelerated wear.[16]Currently in the field of adhesive dentistry, there has been a gratifying swiftness towards the use of newer generation adhesive systems and current generation LED units.

Only few studies have investigated the degree of conversion (DC) of etch-and-bond adhesives,[53] and the kinetic of the polymerization reaction without considering the interactions of the material with the dentinal tissue.[72] The differences in light cure units emission spectrum can have a major effect on the degree of conversion. The proper degree of conversion (DC) of the adhesive is important to their performance. Despite these differences, the influence of light cure units used for light-curing of adhesive systems has seldom been evaluated.

The current study is aimed to calculate the DC of etch-and-rinse(Prime & Bond NT)(PBNT)and one step self-etch adhesives [Beauti Bond(BB), Adper Easy One (EO)and Xeno V(XV)]for LED (Satelec mini LED) and QTH (CU100A) units with the latest adhesive systems compared to two step etch-and-rinse adhesive by FTIR analysis.

In the current study, all the four groups were cured with QTH unit for 10 seconds since it is clinically recommended for curing adhesive systems. With LED unit which has the intensity of 1250mW/cm^2 , all the groups were cured for 10 seconds except in Beauti Bond (group II) was cured for 5 seconds according to the manufacturer's instructions. Generally it is recommended that air-blowing the adhesive layer render a uniform layer

of solvent adhesive resins, and also promote evaporation which was concluded by **Spreafico (2006)** [83].

Ikeda (2005)[41], Nunes (2005)[62] reported that complete evaporation is difficult to achieve in clinically relevant air-blowing times and any remaining solvents may compromise polymerization by dilution of monomers**. Ye et al.(2007)[99]** had also shown that the 'cross linking-facilitated gel phenomenon**'** is suppressed in adhesives with a high solvent content. Nevertheless, in order to standardize procedures, manufacturer's recommended time of about 5 s air-blowing was used in the present study.

In the present study, constant volume of 0.01ml adhesive and light curing was done with the constant distance of 5mm from the KBr pellet for all the samples for standardization. FTIR was used for determining the DC of adhesive systems which provides database of spectra showing "finger print" regions for all the tested samples. This method is a mathematical operation known as Fourier transformation converts the interferogram to the final IR spectrum, that represents the familiar frequency domain spectrum showing intensity versus frequency. In a previous study by **Ye et al.**[99] highly sophisticated time-base collection and FTIR were used to monitor polymerization in real-time **(Ye 2007)**[99] .They showed that polymerization rate differs in different adhesive systems depending on their chemical composition and light source.

The database of point spectra has represented that the "fingerprint" regions for all tissues and materials occur in a range of 200-1800 cm-1. According to **Hsu (1997)[40]** in IR

spectroscopy, all functional groups present vibrational frequencies between 625 cm-1 and 4000 cm-1.

The peak at 1639 cm-1, corresponded with the methacrylate (aliphatic) group, has been located in all dimethacrylate-based monomers, adhesive systems and RBCs. The 1609 cm-1 peak, related with the aromatic group, has been found in BisGMA ,BisEMA based adhesive systems and composites. **Santos (2007)[74], Sadek (2008)[71]** reported that

the change in the ratio of these two peaks has been applied to find the ratio of double bonds after monomer to polymer conversion in adhesives and composites.

In non-BisGMA-based materials, the 1609 cm-1 aromatic peak is most often absent because of the absence of aromatic moieties in the monomers. However, in UDMA based G Bond and Gradia Direct, the presence of the 1609 cm-1 peak may be linked with either functional monomers in the adhesive or additional cross-linking monomers in the composite. **Spencer (2006)[82], Navarra (2009)[59]** reported that in materials where the main cross-linking monomers do not contain aromatic moieties, it is not uncommon to use other groups as the internal standard in DC determinations, such as the C=O group, associated with 1710 cm-1, the CH_2 group, correlated with 1453 cm-1, or the COO group, and associated with 605 cm-1.

The DC for group IV(XV) which is a non BisGMA based adhesive, the carbonyl peak 1710cm-1 peak intensity was observed as internal standard for calculating DC. Each sample was its own control because FTIR spectra contained data from both uncured and cured samples.

LED UNIT > QTH UNIT

The results of the present study showed that higher DC was observed in both the etch-and-rinse and self-etch adhesive system groups with LED unit than QTH cured adhesive samples.

The reasons for better performance of LED can be attributed to the following:

- **Absorption spectrum** of LED curing unit which could be in the range of absorption peak of photoinitiators of the adhesive systems tested . The guiding principle behind the efficiency of a photo activation reaction is the amount of light energy that is absorbed by the photoinitiators during light irradiation. The LED curing unit used in this present study has the spectral wavelength of 420 - 480 nm with the peak wavelength of 455 – 465 nm which is within the useful energy range for activating the photoinitiator camphorquinone (CQ) molecule, most commonly used to initiate the photopolymerization of dental monomer.[66]

The absorption spectrum and particularly the peak absorption wavelength of photoinitiators are considered to be among the main characteristics affecting polymerization. **Van Landuyt (2007)[90]** stated that the spectral emission range of the light source should match the absorption characteristics of the initiator system.

- **Light intensity** is of a great significant factor in the activation of photoinitiator, but more importantly, it is how much of the absorption spectrum of the photoinitiator matches the emitted light effectively. Higher intensity(1250mW/cm^2) of light in LED caused higher degree of conversion in all the tested adhesive samples. The QTH (CU 100 A) unit has the intensity of 500-600mW produced less DC than LED unit.

- The light guide tip of the LED unit used in this study has been designed to **reduce the divergence light** to concentrate the energy of light rays. It makes a reduction of the working surface and at the same time it sustains the lamp's power, allowing efficient polymerization. The more the divergence of light emitted produce less the DC.[76]

Ye et al.[99] used an LED (1200 mW/cm2) and a halogen LCU (300, 550 and 800 mW/cm2) and one etch-and-rinse and two one-step self-etch adhesive systems. The use of LED performed better than the halogen light in terms of polymerization rate and degree of conversion for the commercial single-step, sixth generation adhesive systems.

Xu (2006)[97] **et al.** concluded that a linear correlation between the DC and the light energy density (i.e. light intensity multiplied by curing time) was established in a previous study.

DC after 1 week of dry storage > DC immediately after curing

In the present study, KBr pellet method is used in IR Spectroscopy techniques because it does not absorb moisture at room and it is IR transparent. The proportionally higher degree of conversion was observed consistently in all the groups with both LED and QTH units after 1 week of dry storage of KBr pellets adhesive samples than the conversion obtained immediately after curing confirming the dark curing phenomenon.

The present study result showed, in dry storage, the Prime & Bond NT (group I) show higher DC than Adper Easy One (group III) for LED unit which is not statistically

significant ($p<0.001$). The reason for different behaviour of etch-and-rinse and self-etch adhesives is difficult to explain, not only due to multiple variables but also unknown type and weight percentage of initiator system. The result is in accordance with the previous studies.

Bae et al. (2005)[4] used FTIR spectroscopy, different BisGMA/TEGDMA-based experimental adhesives cured on KBr discs showed higher DC values after 48 hour of storage compared to values obtained immediately after curing.

Dickens et al. (2003)[22] studied on storage of experimental TEGDMA-based RBCs for 24 h in air or distilled water at 37ºC that resulted in significantly higher DC values compared to those obtained 15 min after curing. Similar DC values for the BisGMA/TEGDMA mixture were found irrespective of the storage conditions. TEGDMA-based mixtures containing acidic monomers resulted in comparable of higher DC in dry compared to wet storage conditions.

Sadek et al. (2008)[71] used FT-Raman spectroscopy that resulted in no significant difference in the DC for etch-and-rinse and self-etch adhesives after 24 h storage in dark bottles at 37ºC.

Arrais et al.(2007)[2] reported that there is increase in DC after 1 week storage of adhesive samples in distilled water proving the dark cure phenomenon.

Immediately after curing with LED/QTH light unit & Post polymerization curing after 1 week of dry storage with QTH unit :

Group IV > Group III ≥ Group I > Group II

Post polymerization curing after 1 week of dry storage with LED unit :

Group IV > Group I ≥ Group III > Group II

Among the tested adhesives in the present study, the Xeno V (group IV) shows the highest DC in both LED and QTH light curing units. It is possibly due to the presence of co initiator butylated benzenediol which is not present in other adhesives. The bi functional acrylic amides and inverse functionalized phosphoric acid ester and acryloy amino alkyl sulfonic acid make the adhesive system more hydrolytically stable and the change in the polarity of functional monomer group after curing might be the reason for its higher performance. **Salz (2005)**[73]concluded that methacrylamides have significantly higher hydrolytic stability than methacrylates though their effect on other properties of adhesive systems is still unclear.

Sun (2000)[84] stated that the photo-initiators absorption range may alter depending on the solvent polarity. **Owens & Rodriguez (2007)**[65] concluded that self-etch systems with high solvent content when cured with LED LCUs that exhibit a narrower spectral emission range than conventional halogen LCUs perform better**.** This could be the reason for the highest DC in (group IV) Xeno V than Prime & Bond NT (group I)and (group III) Adper Easy One. The manufacturer's technical data does not mention photoinitiator's

weight or volume of adhesives. Differences in either of weight or volume of photoinitiator may account for the differences in the present results.

The possible differences in the monomer or initiator system in one-step self-etch Adper Easy One Bond system (Group III) could account for higher DC values. The presence of alternative photoinitiators such as trimethylbenzoyldiphenyl phosphine oxide [TPO], which is used in the adhesive which show higher reactivity than CQ has been shown to increase the overall DC of adhesives which is in accordance with **Perdiago et al.(2012)[66] and Borges et al.(2012)[7]** who reported the similar results with Adper Easy One adhesive.

Furthermore, this system contains ethanol as a solvent unlike acetone-based Prime & Bond NT Bond system (Group I) which may alter the monomer chain mobility of the system because of decrease in viscosity.

Since ethanol dilutes the viscous monomers, the reaction occurs in a less restricted environment. According to **Ye et al. (2007)[99]** the decreased viscosity of the system allows propagation to continue for longer times without being diffusion-controlled (i.e., autodeceleration is postponed).The polymerization propagation process then occurs with a postponed autodeceleration phase making its DC values to be reached in a shorter time in one-step Adper Easy One (group III) compared to Prime & Bond NT(group I). An increase in rate of polymerization($R_{p)}$ occurs as the conversion of monomer increases. This is known as auto-acceleration or the Trommsdorf–Norrish effect or the gel effect. Auto-acceleration arises as a consequence of the increase in

viscosity and temperature of the reaction medium caused by the formation of polymer molecules which leads to a rapid decrease in the termination rate-constant (kt).[20]

In the present study, the mean DC of Prime & Bond NT (group I) was less than group IV (Xeno V), group III (Adper Easy One), but no statistical significance with group III. The possible reason could be the presence of PENTA in Prime & Bond NT which is a high molecular weight substance because of a long principal linear organic chain with four lateral chains. This negatively affects the mobility, flexibility and restricts the lateral functional monomers to react. The presence of acetone as solvent in Prime & Bond NT cause dilution of monomers may jeopardize polymerization.

Sarr et al.[75] compared the effectiveness of bonding of 11 commercial dental adhesives and concluded that Prime & Bond NT showed the lesser DC than the tested self-etch adhesives. The reason may be due to difference in composition of the monomer mixture of the tested adhesive.

The role of monomer viscosity in the DC of the methacrylate-based adhesive was previously assayed using mixtures of known compositions: decreasing the viscosity increased the DC.[18,33] The UDMA present in ScotchBond and Amber like Prime & Bond NT used in this study, has higher flexibility even though it has high molecular weight as Bis-GMA and reacts more readily due to its vinyl functional monomer. The –NH– groups of UDMA increase the mobility of radical sites of the polymer network[78].

Beauti Bond (group II) showed the lowest degree of conversion compared to other groups which could be due to presence of acetone and water. The thinner the adhesive

layer the less is the DC. In another study by **Viviane Hass et al.(2012)[92],** among Adper Easy One ,Clearfil S3 Bond and Go evaluated, Go is the only one that contains acetone and water as solvent, which may lead to the formation of a very thin hybrid layer. The thinner the adhesive layer, the more susceptible it is to polymerization inhibition by oxygen, which could be a possible reason for the lower performance of this material.

Navarra et al.[59] also observed that the acetone-based adhesive tested showed lower in situ DC than the two other ethanol-based adhesives tested. Moreover the manufacturer did not reveal the information about the initiators used in this adhesive system. (group II).There are only two studies on Beautibond where **Khoroushi et al.[47](2012) and Hashimoto et al.[38,39](2009)** investigated the marginal sealing ability and bond strength and concluded the higher performance of Beauti Bond which conclude that they perform better.

When adhesives are applied to dentin, it showed substantially higher DC than when applied to glass slides. The importance of substrate is another factor influencing DC of adhesive systems in addition to LCU, curing parameter or chemical composition of adhesive system. In the present study using FTIR, adhesive systems were applied to KBr pellet surface, but not to dentin. Adhesive systems especially self-etch adhesives are designed to be self limiting which means that the original chemical composition changes during interaction with dentin.

Within the limitations of the methodology employed in this in vitro study, the degree of conversion of adhesive resins is dependent on many factors, such as monomer

structure, type of light cure units, light intensity, wave length and curing mode of the light cure units, curing time and curing distance from the material..The results of this study is in accordance with **Faria-e- Silva et al. [30] (2010)** concluded that the impact of LED and QTH lights on the DC of bonding agents was material dependent.

SUMMARY

This study was undertaken to determine the degree of conversion of one etch-and-rinse adhesive (Prime & Bond NT) and three one-step self-etch adhesives (Beauti Bond, Adper Easy One, and Xeno V) for LED and QTH light cure units by Fourier Transform Infrared Spectroscopy (FTIR) analysis, immediately after curing and after one week of dry storage.

For calculating the degree of conversion, KBr pellets were prepared. A constant volume (0.01ml) of adhesive applied on the surface of the pellet. The adhesives were divided into 4 groups each containing 20 samples.

Group I - Prime & Bond NT(Etch-and-Rinse)(Control)

Group II - Beauti Bond

Group III - Adper Easy One

Group IV - Xeno V

The samples were light cured with LED and QTH light cure units with a constant distance of 5mm from the pellet surface - 10 samples per light source in each group.

The degree of conversion was calculated using the formula

Degree of Conversion = (1 – R cured / R uncured) X 100

where R is the ratio of aliphatic and aromatic peak intensities at 1639 cm-1 and 1609 cm-1 in cured and uncured BisGMA-based systems and the ratio of aliphatic and carbonyl peak intensities at 1639 cm-1 and 1720 cm-1 in non-BisGMA-based systems.

The internal standards in BisGMA-based and non-BisGMA-based systems were the aromatic peak at 1609 cm-1 and the carbonyl peak at 1720 cm-1, respectively.]

Statistical analysis was performed using one way ANOVA test, followed by Post-hoc multiple comparisons by Tukey HSD test and paired t test and concluded that LED showed higher degree of conversion than QTH unit in all the groups.

Group IV (Xeno V) showed the highest degree of conversion than other groups. Whereas Group I Prime & Bond NT (etch-and-rinse) and Group III (Adper Easy One) showed no statistically significant difference in degree of conversion and Group II(Beauti Bond) the least degree of conversion.

There is increase in degree of conversion after 1 week of dry storage in all the groups indicating the continuation of polymerization reaction.

CONCLUSION

From the overall results of this in vitro study following conclusions can be arrived.

- ✓ Higher DC is achieved with the LED unit compared with the conventional QTH light cure unit. The more efficient curing regime can be considered advantageous in curing of adhesives in clinical practice.
- ✓ The higher DC was observed after 1 week than immediately after curing in all the groups, confirming the continuation of polymerization reaction.
- ✓ The newer one step self-etch adhesive Xeno V produced the highest DC among the tested adhesives. The Prime & Bond NT and Adper Easy One showed no statistically significant differences in DC whereas Beauti Bond showed the least DC.
- ✓ The combination "bonding agent and curing unit" had a significant effect on degree of conversion.

It is recommended to investigate the effect of QTH and LED curing unit on DC of different adhesive systems in dentin to firmly conclude the present results. On account of continuing development of newer tailor made adhesive systems and its variation in performance with the different type of light cure units have raised the necessity of further studies to investigate in this elite context.

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